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Essential Oils

Their Properties, Identification and Analysis

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by

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AMHERST, MASSACHUSETTS.

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PRELIMINARY STATEMENT.

The following thesis is written in the form of a "Laboratory Guide in Essential Oils" with the intention of publishing it as such.

The work performed in the laboratory consists of the compilation of the methods and the actual performance of them in full. All special reagents were prepared and all identification products isolated, and the physical and chemical properties determined. All of the artificial perfumes were likewise prepared with two exceptions, viz., Aubépine and Coumarine.

The arrangement and compilation is that of the author, and the tables have either been practically rewritten or are wholly new.

PREFACE.

In publishing this laboratory guide it is the desire of the author to place in the hands of students of essential oils a comprehensive set of directions for a preliminary study of the subject.

The course represents information gathered from many authorities supplemented and expanded as the author's experience has dictated.

In developing the subject it has been the constant aim to teach general methods. Those oils have been selected which are typical, and with whose chief constituents the student should become familiar.

Good quality oils may be obtained either from Antoine Chiris Co., or Fritsche Bros., both of New York City.

The course assumes that the student has a good working knowledge of organic chemistry, and is intended to be covered either in the senior or in the first post-graduate year.

In conclusion the author wishes to express his thanks to Dr. J. S. Chamberlain of the Massachusetts Agricultural College for many valuable suggestions and kindly criticisms.

It would give the author pleasure to correspond with teachers who may use the book, and to receive from them or others interested suggestions or criticisms.

R. G. Gates.

Abbreviations:

D_{15} = Specific gravity at 15° C.

$n_{D_{20}}$ = Specific refractive index at 20° C.

a = Optical rotation.

a_D = Specific rotation.

Sol. = Solubility.

B.Pt. = Boiling point.

M.Pt. = Melting point.

Boiling Points of Common Solvents:

Acetic acid,	D =	1.080	B.Pt. =	118° C.
Acetic anhydride,	"	1.073	"	137° C.
Acetone,	"	.792	"	56° C.
Alcohol, ethyl,	"	.783	"	78° C.
Alcohol, methyl,	"	.796	"	66° C.
Benzene,	"	.880	"	80° C.
Carbon disulphide,	"	1.262	"	46° C.
Carbon tetrachloride,	"	1.593	"	76° C.
Chloroform,	"	1.526	"	61° C.
Ether,	"	.736	"	35° C.
Ethyl acetate,	"	----	"	75° C.
Glycerine,	"	1.265	"	290° C.
Petroleum ether,	"	----	"	40° to 150° C.
Toluene,	"	.880	"	110° C.

Apothecaries' Fluid Measure.

1 Drop (gtt.) = 1 20 cc.

1 Minim (Min.) = 1 15 cc.

1 Dram (ʒ) = 60 min. = 4 cc.

1 Ounce (℥) = 8ʒ = 1 fluid℥ = 30 cc.

1 Pint (O) = 16℥ = 16 fluid ℥

PART I

Brief Summary of Facts about Essential Oils, with Tables.

There are two principal kinds of vegetable oils, fixed or fatty oils and essential or volatile oils. An essential oil (par excellance) is a fluid of a specific narcotic odor, colorless, highly refractive, easily inflamable and the stain of which on a piece of paper disappears spontaneously. Such an oil is generally a mixture of a hydrocarbon with an oxygenated body and the term is used as a convenient group name for a class of volatile odor bearing substances occurring in various parts of plants and in some animals. It is to these oils that flowers owe their scent and herbs and spices their fragrance.

Essential oils range all the way from mobile liquids,(essential oils,par excellence) to semi-solids,(balsams and resins) and finally to solids,(camphor). They have a strong tendency to pass,by oxidation or polymerization, from liquid to solid form.

Essential oils are secreted in different parts of the plant. In scented flowers, such as the rose, they are concentrated in the petals, whereas in spice producing plants the chief deposit may occur in the leaves or bark as in the cinnamon, or in the fruit as in the nutmeg, or in the root as in orris oil. In still other cases the oil may be distributed throughout the plant as in the pine tres. In animals the oils are always internal secretions.

The part played by essential oils in the life history of the plant is an important one. They participate normally in the work of fertilization and in the formation of seeds, in the course of which they are partially consumed by oxidation in order to supply the energy required for the work of reproduction. They are also capable of being utilized by the plant, particularly when the latter is protected from the light and no longer assimilates the carbon di-oxide of the air with the same intensity. The animal essences fulfill the same general function in the animal that the plant oils do in the plant.

The following is a brief account of the circulation, evolution and genesis of odorous compounds. This is taken from an address delivered recently by Dr. Eugene Charabot before the College of Pharmacy in Philadelphia. Dr. Charabot, who needs no introduction to essential oil men, has spent more than ten years in research on the subject.

"Formation and Circulation of the Odorous Compounds.

The Perfume of the Entire Plant. The odorous kinds of matter make their appearance in the young green organs. They continue to form and accumulate until the flowering period, but with an activity which slackens more or less appreciably. They migrate from the leaf into the stem, and thence into the inflorescence, obeying the laws of diffusion: a portion enters into solution and, by osmosis, penetrates into the stem. On arriving in a medium already saturated with similar products, a portion is precipitated, whilst the rest, consisting of a relatively soluble mixture, continues to diffuse through the membranes and reaches the organs of consumption, particularly the infloresences.

At the time when the work of fertilization is accomplished, a certain quantity of essential oil is consumed in the infloresence. It is possible and even probable that the green organs produce at the same time further quantities of odorous matters: experiment only permits of the determination of the fact that the difference between the production and consumption is expressed by a loss at the period when the functions of the flower are accomplished.

The practical consequence of this last conclusion is that the harvesting of the perfume-yeilding plants should be effected shortly before this consumption takes place, that is, before the act of fertilization.

When this act has been acomplished, the odorous principles appear to descend again into the stem and, generally, into the organs other than the flower, a migration which is probably induced by the desiccation of the infloresences, which involves, other things being equal, an increase in the osmotic pressure and a partial precipitation in situ of the least soluble principles.

The Perfume in the Isolated Flower. There exists as was supposed by J. Passy and as was proved by A. Hesse and his colaborators, two categories of plants: One class continuing to produce odorous matters when placed under conditions such that the vital functions may still be exercised: the other class containing the whole of their odorous principles in the free state and incapable henceforth of producing any further quantity, even though their vitality be not arrested.

Evolution of the Odorous Compounds abd its Mechanism.

The compound ethers(esters) have their origin, in particularly active fashion, in the green portions of the plants, by the direct action of the acids on the alcohols previously formed. This phenomenon of esterification is assisted by a special agent, probably an enzyme of reversible activity. The influences which are capable of modifying the plants so as to adapt them for a more intense chlorophyllian function are favorable at the same time to esterification, because this function is favorable to the mechanical elimination of water. Thus the chlorophyllian function tends to acquire a new significance: it not only assures the fixation by the plant tissues of carbonic acid gas: it not only effects by favoring transpiration, the circulation of the liquids which carry and distribute the principles necessary to the mineral nutrition of the plant, but it also activifies, once the carbon is assimilated, the condensations which enable the passage from a simple chemical structure to one of the innumerable complex structures, the study of which taxes all the ingenuity of the chemists.

When the alcohol is capable of readily parting with the elements of water, it gives rise, together with the compound ethers (esters) to the corresponding hydrocarbon, so that the first transformations which the alcohols undergo are due to phenomena of dehydration.

The phenomena of isomerization: that is, changes of nature without changes of composition, also proceed together with the metamorphosis of the odorous matter.

Lastly, the alcohols and their ethers are actively converted into their oxidation derivatives, particularly when the infloresences appear, in which organs the fixation of oxygen by the tissues is particularly intense.

Genesis of the Odorous Matters.

The sum of my researches, and the interesting observations of M. Hesse, lead to a conception of the genesis of the odorous matters in the plant. A large number of the odorous products, very diverse in their functions and chemical structure, are produced in consequence of the splitting up, with fixation of the elements of water, of principles called glucosides. There is reason to believe that the glucoside which is capable of yeilding the essential oil is formed, or tends to be formed, in the green portions. Most frequently, this glucoside immediately encounters the conditions of environment which are favorable to its decomposition, and then the essential oil appears in the green portions and begins to circulate, evolve itself and play its part. It may even happen that the medium is so favorable to the splitting up of the glucoside that the latter can never be formed: in this case the whole of the essential oil will exist in the free state in the green organs.

In other cases the glucoside only comes in contact with the ferment which is capable of splitting it, in the flower. It will then only be after it has circulated as far as the flower, undergoing in its course more or less profound modifications, that it will be able to liberate the constituents of the essential oil, and the flower alone will be odorous. It is not impossible that,in certain flowers, the medium may be so favorable to the splitting up of the glucoside, that the latter is completely split up as soon as it arrives. The formation of further quantities of essential oil in certain flowers in proportion as the essential oil already formed is removed, would be expected by a phenomenon of chemical equilibrium. The following reaction: Glucoside + Water = Glucose + Essential Oil, would be restricted by the reverse reaction, and a state of equilibrium would be reached when the glucose and the essential oil would amount to a certain proportion. Thus the flowers in question, if left to themselves, would retain a quantity of perfume which would not increase. On the other hand, if the essential oil be removed as fast as it is formed, the decomposition of glucoside would no longer be limited, and it would continue to take place. Consequently, the appearance of a fresh quantity of perfume in the plant whose life is prolonged whilst the odorous matter is continuously removed, follows as the result of a phenomenon of chemical equilibrium in the vegetable cell."

Thus it may be seen that there is a steady progression from the simple to the complex. The chlorophyl absorbes the carbon di-oxide from the air. This carbon di-oxide is itself an acid and by condensation forms hydrocarbons and alcohols, which by further condensation form esters and glucosides.[1] These under the reversible reaction of enzymes are decomposed into sugars and essential oils. Thus the enzymes perform the double function of the esterification of the alcohols to form esters, and of hydrolysis of the glucosides to form a sugar and the complex aromatic bodies which constitute an essential oil.

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[1] The term "glucoside" is applied to all those vegetable products which on treatment with acids, alkalies or enzymes, yield a sugar (glucose) and one or more complex derivatives, i.e., an essential oil.

Classification of Aromatic Substances According to Origin.

From the above, two general sources of scent-bearing products may be observed, viz., the Vegetable Kingdom and the Animal Kingdom. There is still another source which is becoming more and more prominent, viz., Synthetic Chemistry.

Nature of Scent. Smell is caused by a resistance of the olefactory nerves to chemical action and essential oils have been found to possess odor only when in the act of eremacausis, that is, oxidation at ordinary temperatures. The cause, therefore, of odor is the continual though minute oxidation of the olefactory nerves and their consequent stimulation by the very small particles of essential oil floating through the air. As Piesse says, there is probably a "harmony and dissonance" of odors as of sound in music and a law might be deduced for the combination of the different chemical components present in the oils so as to form any desired odor or a series of harmoniously graded scents. Along this line it might be well to call attention to the law governing the relation of color to fragrance. From the most fragrant flowers which are invariably white to the least fragrant which would be theoretically black the order is: white, yellow, red, blue, violet, green, orange, brown, black.

Magnitude of the Essential Oil Industry.

Few people realize the magnitude of the essential oil industry. Each year millions of dollars worth of these oils are gathered from all parts of the world, refined and used in some one of the four major branches of the industry. Cannes, Grasse and Nice in France are the principal sources of our fine perfumes. The annual production from these three points alone is valued at something over a million dollars. The leading product is the Oil of Neroli, of which over 400,000 dollars worth is produced each year. Bulgaria and the Balkans are known as the "Rose Garden of the World". Here, in the rose season, as much as 10,000 dollars worth of the "Attar" is produced in a single day. Japan is the Land of Camphor and England is the Lavender Kingdom while the United States leads in Turpentine and Peppermint, very large acreages of the latter being under cultivation in the states of New York and Michigan. Nor should the work of Synthetic Laboratories be overlooked. The names of DeLaire, in France, Heine & Co., in Germany and the Synfleur Laboratories in the United States are by-words in the perfume industry.

The four main branches of the Essential Oil Industry are those of, Perfumes, Cosmetics, Flavoring Extracts and Pharmacy.

The principal oils used in the making of perfumes are as follows:

Bay, Bergamot, Cassia, Cinnamon, Citronella, Frankinsence, Geranium, Jasmine, Lavender, Lemon-grass, Linaloe, Myrrh, Neroli, Orris, Patchouli, Pettigrain, Rose, Rosemary, Sassafras, Thyme, Verbena, Veti-vert, Ylang-ylang and Pomades of difficultly obtainable oils, e.g. Violet, Mignonette and Tuberose. Also many artificial perfumes and the following animal secretive essences which are used almost exclusively as "fixers"

Ambergris, Castor, Civet, Musk.

In the manufacture of Cosmetics, which may be understood to embrace soaps, skin creams, lotions, powders, hair dyes, etc., the above mentioned oils are used as well as the following substances:

Alloxan, to produce gradually a pink tint on the skin,

Aromatic Benzoic Acid, for fine toilet preparations,

Acetic Acid, for toilet vinegars,

Oxide of Tin, as a nail polish,

Potassium Permanganate, or Chamelion Mineral, to dye hair brown or black,

Pyrogallic Acid, to dye hair black,

Vegetable Dyes which are soluble in essential oils.

The oils used in making Flavoring Extracts include the following:

Absimthe, Allspice, Aniseed, Bitter Almonds, Caraway, Carrot, Celery, Cinnamon, Clove, Ginger, Juniper, Lemon, Lime, Mace, Mustard, Nutmeg, Neroli, Onion, Orange, Parsley, Peppermint, Sage, Sassafras, Spearmint, Sweet Birch, Thyme, Wintergreen.

The oils chiefly in demand in Pharmacopoeal work, to which may be added aromatic spirits of ammonia, are as follows:

Arnica, Asafoetida, Camphor, Cajeput, Cubeb, Eucalyptus, Ginger, Pennyroyal, Peppermint, Rosemary, Tansy, Wintergreen.

The following table of synonymous names for certain oils is given owing to the frequent confusion caused by the use of dual names:

Table I.

Oils having two or more synonymous names. The more common name given first.

Absinthe = Wormwood.   Allspice = Pimento.

Calamus = Sweet Flag Root.   Cassia = Chinese Cinnamon.

Citron = Cederat.   Cumin = Cummin = Roman Caraway.

Frankinsense = Olibanum.   Lemon Grass = Indian Verbena.

Linaloe = Lignaloe.   Mace = Nutmeg (first quality).

Marjoram = Origanum.   Neroli Bigarade = Bitter Orange Flower.

Neroli Portugal = Sweet Orange Flower.

Orange Bigarade = Bitter Orange.   Orange Aurantum = Sweet Orange.

Orris = Iris.

Palmarosa = Indian Geranium = Turkish Geranium.

Petitgrain = Orange-leaf Oil = Petits-grains.

Rose = "Attar" or "Otto" of Rose.

Bois de Rose Femelle = Brazilian Linaloe.

Rosewood = Rhodium = Bois de Rose Male.

Sandalwood = Santalwood.   Vetiver = Veti-vert = Cuscus.

Wintergreen = Gaultheria.

Ylang-ylang = Canauga (first quality).

Table II.

Botanical Classification of Essential Oils.

Class.	Sub-class.	Division.	Natural Order.
Gymnosperms.	—	—	Coniferae.
Angiosperms.	Mono-cotyledons.	—	Gramineae.
			Arcideae.
			Liliaceae.
			Iridaceae.
			Zingiberaceae.
	Di-cotyledons.	Monochlamydeae.	Piperaceae.
			Cannabinaceae.
			Myricaceae.
			Salicineae.
			Chenopodiaceae.
			Laurineae.
			Myristiceae.
			Euphorbiaceae.
			Cupuliferae.
			Santalaceae.
		Gamopetalae.	Labiatae
			Verbenaceae.
			Convolvulaceae.
			Jasmineae.
			Ericaceae.
			Valerianeae.
			Compositae.
			Caprifoliaceae.
		Polypetalae.	Umbelliferae.
			Myrtaceae.
			Rosaceae.
			Leguminosae.
			Saxifragaceae.
			Hamamelideae.
			Terebinthaceae.
			Geraniaceae.
			Tropoeoleae.
			Rutaceae.
			Zyngophylleae.
			Anacardiaceae.
			Buseraceae.
			Tiliaceae.
			Malvaceae.
			Ternstroemiaceae.
			Clusiaceae.
			Dipterocarpeae.
			Polygalaceae.
			Cruciferae.
			Resedaceae.
			Turneraceae.
			Cistineae.
			Ranunculaceae.
			Magnoliaceae.
			Anonaceae.

Table III

Physical and Chemical Constants of Essential Oils.

Oil.	Cost lb.	Botanical Derivation	Chief Constituents.	Nativity.	Yeild per.cent.	D_{15}	$N_{D,20}$	a_D	Sol.in Alcohol.
Allspice	1.85	Fruit, Pimenta officinalis	Eugenol, 65 p.c.	West Ind.	3 - 4.5	1.030- 1.055	1.510- 1.533	-1 - +4	1 : 2 pts. 70 p.c.
Angelica	34.00	Root, Angelica officinalis	D-Phellandrene Methyl-ethyl acetic ac.	Scandinavia	1 - 1.2	.860- .905	1.480-	+18 - +30	——
Anise	2.75	Fruit, Pimpinella anisum	Anethol, 80 p.c. Methyl clavicol	Asia Minor China	2.5 - 5.0	.980- .990	1.552- 1.558	0 - -2	1 : 3 90 p.c.
Arnica	384.00 flowers	Root, Arnica Montana	Di-methyl thymoquinol 80 Phlorol iso-butyrate 20	Swiss Alps	.5 - 1.0	.990- 1.00	——	-1 - -2	——
Asafoetida	24.00	Resin, Asafoetida ferula	$C_7H_{14}S_2$,45,$C_{10}H_{20}S_2$,20 $C_{10}H_{16}O)_n$,20	Turkestan	3.3 - 3.7	.975- .990	——	-10	1 : 10 70 p.c.
Bay	3.00	Leaf, Pimenta acris	Eugenol, 65 p.c. Clavicol	West Ind.	2.3 - 2.5	.965- .995	1.487- 1.585	0 - -2	1 : 1 90 p.c.
Bergamot	6.50	Fruit, Citrus bergamia	Linalyl acetate, 35 p.c Limonene,45,Linalol,14	So. Italy	variable	.882- .886	1.465- 1.470	+8 - +20	1 : 2 80 p.c.
Bitter Almond	4.00	Fruit, Amygdalus communis	Benzaldehyde,95 p.c. Hydrocyanic acid, 3 p.c	Germany	.5 - 1.0	1.045- 1.070	1.542- 1.550	0	1 : 2 70 p.c.
Buchu	32.00	Leaf, Betulina barosma	Diosphenol, 90 p.c.	So.Africa	1.0 - 2.0	.940- .945	1.480	+60	——
Cajuput	.55	Leaf, Melaleuca	Cineol, 60 p.c.	Malay	——	.917- .930	1.465- 1.468	0 - -3	1 : 1 80 p.c.
Calamus	2.10	Root, Calamus acorus	Asarone Eugenol	Europe Asia	1.5 - 3.5	.960- 1.00	1.507- 1.515	+10 - +35	1 : 1 90 p.c.
Camphor Oil	.14	Wood, Camphor officinalis	Camphor, 25 p.c. Safrol, 50 p.c.	Japan	4.0	.895- .959	1.460	+12 - +32	——
Canauga	3.50	Flower, Canauga odorata	Geranyl and Linalyl esters	Philippine Islands	——	.896- .942	1.478- 1.508	-27 - -87	1 : 1 95 p.c.
Caraway	1.05	Seed, Carum cari	Carvone, 50 p.c. Limonene, 50 p.c.	England Holland	3.0 - 7.0	.905- .920	1.487- 1.497	+70 - +85	1 : 10 80 p.c.
Cardamon (Malabar)	32.00	Fruit, Cardamon elletaria	Cineol, 10 p.c. Terpineol	India Ceylon	2.0 - 8.0	.936- .946	1.460- 1.470	+26 -+47	1 : 4 70 p.c.
Cascarilla	20.00	Bark, Croton eleutharia	Cascarillic acid, 2 p.c Terpenes	Bahama Islands	1.5 - 3.0	.890- .930	1.489	+5	1 : 1 90 p.c.
Cassia	.87	Bark, Cassia cinnamomum	Cinnamic aldehyde,80 pc	China	.2 - 1.9	1.050- 1.065	1.585- 1.605	+1 - -1	1 : 2 80 p.c.
Cedar-wood	.14	Wood, Juniper-	Cedar camphor, 10 p c Cedrene, 80 p.c.	Florida	2.5 - 4.5	.940-	1.498-	-25 - -40	1 : 5

Table III

Physical and Chemical Constants of Essential Oils.

Oil.	Cost lb.	Botanical Derivation	Chief Constituents.	Nativity.	Yeild per cent.	D_{15}	$N_{D,20}$	a_D	Sol. in Alcohol.
Celery	12.00	Seed, Apium graveolens	Limonene, 60 p.c. Sedanolide	Temperate Climates	2.5 - 3.0	.870- .895	1.475	+65 - +80	1 : 10 90 p.c.
Chamomile (Roman)	16.00	Flower, Anthemi is nobilis	Amyl tiglate + Hexyl angelate, 80 p.c.	Germany Italy	.8 - 1.0	.905- .915	1.445	+1 - 3	1 : 6 70 p.c.
Cinnamon	9.00	Bark, Cinnamo- mum zeylanicum	Cinnamic aldehyde,70 pc Eugenol, 6 p.c.	Ceylon	.5 - 1.0	1.025- 1.040	1.590- 1.599	0 - -1	1 : 2 70 p.c.
Citronella	.42	Leaf, Cymbopog on nardus	Citronellal, 50 p.c. Geraniol, 40 p.c.	Ceylon	Variable	.885- .920	1.465- 1.468	0 - -16	1 : 3 80 p.c.
Citron	4.00	Peel, Citrus medica	Citral and Limonene	Italy France	"	.860- .870	1.475	+66 - +76	———
Clove	1.40	Bud, Eugenia caryophyllata	Eugenol,85; Eugenyl ace tate,10; Caryophyllene5	Zanzibar	15 - 18	1.049- 1.065	1.530- 1.535	0 - -1.3	1 : 1.5 70 p.c.
Cognac	80.00	Wine lees	Ethyl oenanthylate,75 Butyl alcohol, 13 p.c.	France	.3 - .5	.876- .883	———	-.05 -+.75	1 : 3.5 80 p.c.
Copaiba	1.25	Resin, Copai- fera Lansdorfii	Caryophyllene	Bahia Maracaibo	40.0 - 80	.900- .910	1.500- 1.510	-5.0 - -35	1 : 10 95 p.c.
Coriander	6.00	Seed, Corian- der sativum	d-Linalol, 50 p.c. Pinene	Russia Levant	.2 - 1.0	.870- .885	1.466-	+7 - +14	1 : 3 70 p.c.
Costus	72.00	Root, Aplotaxis lappa	Iso-irone, 10 p.c.	E India	1.0	.980- .987	———	+15 - +16	1 : .5 90 p.c.
Cubeb	3.40	Fruit, Piper cubeba	Cadinene, 50 p.c. Dipentene	Java	10 - 18	.910- .930	1.490- 1.496	-30 - -40	1 : 1 95 p.c.
Cumin	4.75	Fruit, Cumin- um cymium	Cymene Cumic aldehyde	India Sicily	2.5 - 4.0	.890- .930	———	+4 - +8	1 : 5 80 p.c.
Cypress	12.00	Leaf, Cypress- us sempervirens	Pinene Cypress camphor	Generally	1.0	.866- .887	1.474	+4 - +26	1 : 4 90 p.c.
Dill	4.00	Fruit, Anethum graveolens	Phellandrene, Terpinene Carvone	England Germany	2.0 - 4.0	.900- .920	1.480- 1.495	+70 - +80	1 : 6 80 p.c.
Eucalyptus	1.00	Eucalyptus globulus	Eucalyptol, 65 p.c. Pinene	Australia	.8 - 3.0	.910- .930	1.460- 1.467	+1 - +10	1 : 3 70 p.c.
Fennel	1.65	Fruit, Foenic- ulum vulgare	Fenone, 12 p.c.	So. Europe	1.0 - 6.0	.960- .980	1.525- 1.534	+6 - +20	1 : 1 90 p.c.
Fir-cone	.60	Cones, Abies alba	Pinene, 52 p.c.,Limonene 37 p.c.,Bornyl acetate5	Arcadia	———	.860- .875	———	-20 - -80	1 : 6 90 p.c.

Table III (continued).

Oil.	Cost lb.	Botanical Derivation.	Chief Constituents.	Nativity.	Yeild per cent.	D_{15}	$N_{D,20}$	a_D	Sol.in Alcohol
Galangal	14.00	Root, Alpinia galanga	Eugenol, 25 p.c. Cineol	China Siam	.5 - 1.5	.915- .925	1.480	-1 - -4	1 : .5 90 p.c.
Garlic	48.00	Herb, Allium sativum	Di-allyl, sulphide, 60p.c Allyl-propyl di-sulph.6	Temperate climates	.007-.09	1.046- 1.057	——	0.	——
Geranium	8.50	Pelargonium odoratissimum	Geraniol, 65; Geranyl acetate, 25; Citronellol, 25	So. Europe Algeria	.18	.888- .905	1.460- 1.471	-6 - -16	1 : 3 70 p.c.
Geranium (Indian)	4.00	Grass, Cymbopogon Martini	Geraniol, 75 p.c. Di-pentene	India	.30	.885- .896	1.485- 1.492	+2 - -2	1 : 3 70 p.c.
Ginger	6.50	Root, Zingiber officinallis	Phellandrene l-zingiberene	E. India W. Indies	2.0 - 3.0	.872- .885	1.488- 1.495	-25 - -45	1 : 100 95 p.c.
Ginger Grass	3.50	Grass, Cymbopogon Family	Di-hydro cumic aldehyde 85 p.c., Geraniol	India	.40	.930- .945	1.485	+18 - +27	1 : 1 90 p.c.
Golden Rod	8.00	Herb, Solidago Canadensis	Pinene, 85, Borneol, 10, Bornyl acetate 4 p.c.	Canada U.S.	.30	.850	1.485	-11	1 : 3 95 p.c.
Guaiacum Wood	2.00	Wood, Guaiacum Bulnesia	Guaiol 80 p.c.	Argentine Paraguay	4.0 - 8.0	.965- .975	——	-6.5 (-30°)	1 : 3 70 p.c.
Gurjun Balsam	.50	Balsam, Dipterocarpus	Sesqui-terpenes	So. America	40 - 70	.910- .930	——	-35 - -106	slightly 95 p.c.
Hedeoma	2.75	Herb, Hedeoma pulegoides	Menthone, 50 p.c. Pulegone, 30 p.c.	No. America	1.5 - 3.0	.925- .940	——	+18 - +22	1 : 2 70 p.c.
Hemlock	.55	Abies Canadensis	Pinene, 52 p.c. Bornyl acetate, 36 p.c.	Canada	——	.907- .913	——	-21 - -24	——
Jasmine	128.00	Flower, Jasminum grandiflorum	Benzyl & Linallyl acetates, 70, Jasmone	So. France	Very small	1.009- 1.018	——	+2.3 - +3.3	1 : 150 70 p.c.
Juniper Berry	.90	Berry, Juniperus communis	Pinene, 30 p.c. Cadinene 15 p.c.	Italy	.6 - 1.5	.865- .900	1.474- 1.488	-4 - -12	1 : 4 95 p.c.
Kuromoji		Herb, Lindera sericea	d-Limonene, Terpineol, l-Carvone	Japan	——	.890- .915	——	-.1	——
Laurel	.35	Leaf, Laurus nobilis	Pinene, Eugenol, Cineol	No. America	1.0 - 3.0	.920- .930	——	-15 - -18	1 : 3 80 p.c.
Lavender	4.00	Flower, Lavendula vera	Linallyl acetate (Eng) 7-10, (Fr) 25-40	England Switzerland	Variable	.885- .900	1.462- 1.467	-3 - -10	1 : 3 70 p.c.
Lemon	4.00	Peel, Citrus limonum	Citral, 6 p.c. d-Limonene	So. Europe	"	.857- .862	1.475- 1.477	+59 - +65	——
Lemon Grass	1.50	Grass, Cymbopogon citratus	Citral, 80 p.c. Geraniol	Ceylon Malabar		.877- .905	1.483- 1.488	+3 - -3	1 : 2 70 p.c.
Lime	.60	Fruit, Citrus limetta	Linallyl acetate, 26p.c Citral, 8 p.c.	Italy W. Indies		.870- .875	1.475- 1.485	+35 - +40	——

Table III (continued).

Oil	Cost lb.	Botanical Derivation	Chief Constituents	Nativity	Yeild per cent.	D_{15}	$N_{D,20}$	a_D	Sol. in Alcohol
Linaloe	3.00	Wood, Bursera delpeckiana	Linalol,90 p.c., Geraniol,2 p.c.,m-Heptanone.1	Mexico	7.0 - 9.0	.872-.895	1.464	-4 - -13	1 : 2 70 p.c.
Lovage	60.00	Root, Levisticum officinalis	d-Terpineol	Germany Italy	.1 - 2.0	1.005-1.045	——	+2 - +7	1 : 3 80 p.c.
Mace	1.00	Fruit, Myristica fragrens	Pinene + Camphene,80p.c Myristicin, 4 p.c.	Sumatra Spice Is.	4.0 - 15	.890-.932	1.476-1.484	+10 - +20	1 : 3 90 p.c.
Marjoram	7.25	Herb, Origanum marjorana	Terpineol, 60 p.c. Terpinene, 40 p.c.	So.Europe	.3 - .9	.890-.910	1.475-1.485	+15 - +20	1 : 2 80 p.c.
Mustard	6.00	Seed, Sinapis nigra	Allyl iso-thio-cyanate, 92 p.c.	No.America	Variable	1.014-1.032	1.525-1.535	0 - +1	1 : 10 70 p.c.
Myrrh		Communiphora myrrha	——	India	2.0 - 10	.988-1.007	1.536	-67 - -90	1 : 10 90 p.c.
Neroli	35.00	Orange flowers	Linalyl acet.14,Linalol 20,Limonene,50,M-Anthranilate,.7	So.France	.1	.800-.870	1.475	+15 - +25	1 : 2 80 p.c.
Nutmeg	.75	Fruit, Myristica fragrans	Pinene + Camphene,80p.c Myristicin, 4 p.c.	Sumatra	8.0 - 15	.865-.920	1.476	+14 - +30	1 : 3 90 p.c.
Orange	3.00	Peel, Citrus bigarade&aurantium	Limonene, Linalyl acetate, Citral	So.Europe	Variable	.847-.853	1.472-1.478	+92 - +98	1 : 4 95 p.c.
Orris	80.00	Root, Iris	Irone, 10 p.c. Myristic acid, 90 p.c.	So.Europe	.1 - .2	.949	——	+15 - -28	1 : 10 96 p.c.
Parsley	5.50	Seed, Petroselinum sativum	Apiol, 1-Pinene	Germany France	2.0 - 6.0	1.050-1.100	1.489	-5 - -10	——
Patchouli	3.25	Leaf, Pogostemon patchouli	Patchoulyl alcohol Eugenol	Java Singapore	1.5 - 4.0	.975-.995	1.512	-50 - -68	1 : 1 90 p.c.
Pennyroyal	2.00	Herb, Mentha pulegium	Pulegone, Menthone	Europe Chili	1.5 - 3.0	.930-.960	1.481-1.483	+16 - +25	1 : 2 70 p.c.
Peppermint	2.85	Herb, Mentha piperita	Menthol, 48 - 64 p.c.	U.S.,Japan England	.1 - 1.5	.900-.920	1.465	-18 - -33	1 : .5 90 p.c.
Petitgrain	6.00	Leaf, C. bigarade & aurantium	Linalyl acetate,70,Linalol,30,Limonene	Paraguay	——	.885-.900	1.462-1.464	-2 - +5	1 : 2 80 p.c.
Pine-needles	2.75	Needles, Pinus pumilio	1-Limonene,70,1-Pinene, 30 p.c.,Bornyl acetate	Temperate Climates	.1 - .8	.859-.865	——	-3 - -10	1 : 6 90 p.c.
Rose	256.00	Flower, Rosa Damascena	Geraniol,70 p.c. Citronellol	France Bulgaria	.02	.853-.858	1.458-1.400	-1 - -4	1 : 30 70 p.c.
Rosemary	1.10	Flower,Rosmarinus officinalis	Borneol,10 p.c.,Bornyl acetate,2 p.c.,Cineol	So.Europe	.4 - 1.0	.896-.920	1.466-1.471	-9 - +18	1 : 1 90 p.c.
Rose-wood	16.00	Wood, Convolvulus Floridus	Sesqui-terpenes,80 p.c.	Canary Is.	——	.900-.910	——	-15	——

Table III (continued).

Oil.	Cost lb.	Botanical Derivation.	Chief Constituents.	Nativity.	Yeild per cent.	D_{15}	$N_{D,20}$	a_D	
Rue	4.50	Herb, Ruta graveolens	Methyl-nonyl ketone,90 Lauric aldehyde	Germany Algeria	——	.832- .641	1.435- 1.440	0 - +3	1 : 3 70 p.c.
Sage	2.50	Leaf, Salira officinalie	Cineol, Thujone, Pinene	Germany	1.5 - 2.5	.910- .930	1.462	+10 - +25	1 : 2 80 p.c.
Sandal-wood	5.75	Wood,Santalum album	Santalol,90 - 95 p.c.	India	1.6 - 5.0	.973- .985	1.505- 1.510	-12 - -20	1 : 5 70 p.c.
Sassafras	.58	Wood, Sassafras officinalis	Safrol,80 p.c.,Pinene, 10 p.c.,Cadinene,3 p.c.	No.America	7.0 - 8.0	1.065- 1.095	1.525- 1.535	+1 - +4	1 : 1 90 p.c.
Spear-mint	4.75	Herb, Mentha viridis	Carvone, 56 p.c., Limonene, 45 p.c.	No.America	.22 - .30	.920- .980	1.488	-30 - -50	1 :1 90 p.c.
Spike-lavender	1.00	Flower, Lavendula spica	Linalol, 40 p.c.,Cineol	Switzerland	.5 - 1.0	.905- .920	1.466- 1.468	-3 - +7	1 : 6 65 p.c.
Sweet-birch	1.50	Bark, Betula lenta	Methyl salicylate,99.8	No.America	.60	1.180- 1.187	1.535	0	1 : 5 70 p.c.
Sweet-basil	18.00	Herb, Ocymum basilicum	Cineol, Linalol, Methyl clavicol	Germany Reunion	1.5	.900- .930	1.481	-20 - +12	1 : 2 80 p.c.
Tansy	4.00	Herb, Tanacetum vulgare	Thujone, Camphor, Borneol	England Germany	.1 - .3	.925- .950	1492	-25 - +45	1 : 3 70 p.c.
Thyme	1.30	Herb, Thymus vulgare	Thymol + Carvacrol,50pc	France	.3 - 2.6	.900- .950	1.480- 1.490	——	1 : 2 80 p.c.
Turpentine (American)	.25 (rect.)	Wood, Pinus Australis	Pinene, 90 - 95 p.c.	Georgia No.Carolina		.855- .870	1.470- 1.475	+10 - +15	1 : 3 95 p.c.
Valerian	5.50	Root, Valeriana officinalis	Borneol, Bornyl acetate	Japan	6.0 - 7.0	.985- .995	1.485	-8 - -15	——
Verbena	6.00	Verbena officinalis	Citral, 15 - 35 p.c. Limonene	So.Europe		.890- .900	1.487	-16 - +3.0	1 : 5 90 p.c.
Vetiver	32.00	Grass, Vetiveria zizanoides		India	.4 - .9	1.010- 1.030	——	+25 - +40	1 : 2 80 p.c.
Winter-green	4.50	Bark, Gaultheria procumbrens	Methyl salicylate 99 p.c	No. Amer.	.75	1.177- 1.187	1.531- 1.538	0 - -1	1 : 6 70 p.c.
Worm-wood	6.00	Herb, Artemisia absinthium	Thujone, Thujyl alcohol Phellandrene	No.America No.Asia	.2 - .9	.925- .955	1.460- 1.470	——	1 : 3 80 p.c.
Ylang-ylang	30.00	Flower, Canauga odorata	Geranyl and Linalyl esters	Philip.Is.	Very small	.930- .950	1.493- 1.496	-30 - -45	1 : 40 70 p.c.

Table III (continued).

Animal Secretive Essences

Oil	Cost lb.	Derivation.	Chief Constituents.	Nativity.	Yeild per cent.	D_{15}	$N_{D,20}$	a_D	Sol. in Alcohol.
Ambergris (gray)	400.00	Pot-whale	Ambrein	Ind.Ocean		.780-			
Castor	20.00	Beaver	Salicin, Phenic acid, Castorin, Bile.	No.America	1.0 - 2.0				1 : 6 90 p.c.
Civet	25.60	Civet-cat Musk-rat		Asia No.America					
Musk	400.00	Musk-deer Alligator	Muskone	Asia Tropics	1.4				

Table IV

Chief Constituents of Essential Oils and Occurrence. Chemically Classified.

Classification.	Constituent.		Chief Natural Occurrence.
Hydrocarbons C_nH_{2n}	Paraffins, (Olefines)		Rose, Geranium,
	Cymene	$C_{10}H_{14}$	Wild Thyme, Cumin.
Hydrocarbons C_nH_{2n-4}	Pinene,	$C_{10}H_{16}$	Turpentine, Laurel,
(Terpenes)	Limonene,		Lemon, Orange, Bergamot.
	Di-pentene,	"	Turpentine, Cubeb, Thyme.
	Phellandrene,	"	Bitter-fennel, Eucalyptus.
	Sylvestrene,	"	Turpentine (Russian & Sweedish).
	Terpinene,	"	Cardamoms.
	Camphene	"	Rosemary, Camphor oils.
	Thujene,	"	Thuja oil.
Hydrocarbons C_nH_{2n-6}	Caryophyllene,	$C_{15}H_{24}$	Cloves.
(Sesqui-terpenes)	Cadinene,	"	Cade, Patchouli, Galbanum.
	Santalene,	"	Sandal-wood.
	Cedrene,	"	Cedar.
	Zingiberene,	"	Ginger.
Alcohols $C_nH_{2n-2}O$	Geraniol,	$C_{10}H_{17}OH$	Rose, Geranium, Palmarosa.
(Terpene-olefinic)	Linalol,	"	Linaloe, Lavender, Bergamot.
	Nerol,	"	Neroli, Petitgrain.
	Citronellol,	$C_{10}H_{19}OH$	Rose, Geranium.
Alcohols $C_nH_{2n-2}O$	Borneol,	$C_{10}H_{17}OH$	Rosemary, Borneo-camphor.
(Terpene-cyclic)	Cineol,	"	Eucalyptus, Cajuput.
	Terpineol,	"	Cardamon, Marjoram.
	Menthol,	$C_{10}H_{19}OH$	Peppermint.
Alcohols	Benzyl alcohol	C_7H_7OH	Jasmine, Peru-balsam.
(Benzene series)	Styryl alcohol	C_9H_9OH	Storax.
Phenols	Eugenol,	$C_{10}H_{12}O_2$	Clove, Allspice, Bay.
	Safrol,	$C_{10}H_{14}O$	Sassafras, Camphor-oil.
	Thymol,	"	Thyme, Ajowan.
	Anethol,	$C_{10}H_{12}O$	Anise.
	Carvacrol,	"	Marjoram, Satureja.
	Clavicol,	$C_9H_{10}O$	Betel.
	Diosphenol,	$C_{10}H_{16}O$	Buchu.
Aldehydes $C_nH_{2n-4}O$	Citral,	$C_{10}H_{16}O$	Lemon, Lemon-grass.
(Terpene-olefinic)	Citronellal,	$C_{10}H_{18}O$	Lemon, Citronella.
Aldehydes	Benzaldehyde,	C_7H_8O	Bitter-almond, Cherry-laurel.
(Benzene series)	Cinnamic ald.	C_9H_8O	Cinnamon, Cassia.
	Salicylic ald.	C_7H_6O	Spiroea.
	Anisic ald.	$C_8H_8O_2$	Anis-seed, Fennel.
	Cumic ald.	$C_{10}H_{12}O$	Roman Caraway.
	Vanillin,	$C_8H_8O_3$	Vanilla, Beet-root, Asparagus.
	Heliotropin,	$C_8H_6O_3$	Heliotrope.
Acids	Benzoic,	$C_7H_6O_2$	Benzoin.
(Benzene series)	Cinnamic,	$C_9H_8O_2$	Storax.
	Coumaric,	$C_9H_8O_3$	Tonka-bean.
	Coumarin,	$C_9H_6O_2$	Tonka-bean, Deer's tongue.

Table IV (continued).

Classification.	Constituent.	Chief Natural Occurrence.
Ketones (Cyclic)	Carvone, $C_{10}H_{14}O$	Caraway, Spearmint, Dill.
	Menthone, $C_{10}H_{18}O$	Peppermint, Hedeoma.
	Pulegone, $C_{10}H_{16}O$	Hedeoma, Mountain-mint.
	Irone, $C_{13}H_{20}O$	Orris-root, Violet.
	Thujone, $C_{10}H_{16}O$	Absinthe, Tansy.
	Fenchone, "	Fennel.
	Camphor, "	Camphor, Laurel, Sassafras.
Esters (Terpene-olefinic)	Geranyl acetate $C_{12}H_{20}O_2$	Geranium.
	Linalyl acetate "	Lavender, Bergamot.
Esters (Terpene-cyclic)	Bornyl acetate $C_{12}H_{20}O_2$	Rosemary, Golden-rod.
	Menthyl acetate $C_{12}H_{22}O_2$	Peppermint.
Esters (Benzene series)	Methyl salicylate $C_8H_8O_3$	Winter-green, Sweet-birch.
	Benzyl acetate $C_9H_{10}O_2$	Jasmine.
Sulphides (Benzens series)	Allyl-propyl di-sulphide	Garlic, Onion.
	Di-allyl sulphide	Garlic.
	Vinyl sulphide	Allium oil
	Allyl iso-thio-cyanate	Mustard, Horse-radish.
Nitrogen Compounds	Prussic acid, HCN	Bitter-almond, Cherry-laurel.
	Cyan-hydrine of Benzaldehyde, C_8H_7ON	Bitter-almond.
	Pyrrole, C_4H_4NH	Oil of Unripe Oranges.
	Indole, C_7H_7N	Jasmine.
	b-phenyl propionic nitrile C_9H_9N	Water-cress.

General Characteristics of Essential Oils.

1. Specific gravity, with few exceptions, = .850 - .900
2. High refractive index, = 1.4600 - 1.5100
3. Optically active except in a few rare cases.
4. Volatile at ordinary temperatures.
5. Many of them deposit Stearoptenes on cooling.
6. Sparingly soluble in water, (not over 2.2 grams per liter),
7. Freely soluble in alcohol, ether and carbon di-sulphide.
8. Characteristic aroma and medicinal properties, due almost entirely to oxygenated compounds and not to the terpenes.

Extraction of Essential Oils.

1. By expression, (Lemon, Bergamot).
2. By distillation with steam. This is the most common method and applies to nearly all oils.
3. Enfleurage, or solution in a fixed oil devoid of odor, to form a pomade. This is the common method of extracting all oils of delicate odor and present in very small amounts, (Jasmine, Violet, Mignonette, Tuberose).
4. Extraction with volatile solvents and the recovery of the oil by the evaporation or distillation of the solvent.

Table V.

Plants and Flowers of Peculiar Odor.

Botanical Classification.	Nativity.	Part of Plant.	Character of Odor.
Clitophilus sinuata		Fungus	Burnt sugar.
Tricholoma myomyces		"Mouse-mushroom"	Mice.
Astragalus caprinus	Barbary	Legumes	Goats.
Orchis coriophora			Disgusting odor of bugs.
Psoralia bituminosa	Languedoc	Leaves	Tar.
Spiroea ulmaria		Leaves	Carbolic acid.
Helleborus foetidus	Common		"Stinking Hellebore", Dung.
Anagyris foetida	So.Europe	Whole tree	Human feces. (attracts flies).
Arum aracunculus	So.Africa	Great Carrion Flower, (liver colored)	Carrion. (attracts crows).
Saussurea	Alps	Thistle	Putrid meat.
Marchella		Fungus	Roast beef.
Rhus aromatica	America	Sumac bark	Bed-bugs.
Chenopodium olidum	Common	Whole plant	Decayed fish, (crabs, herring).
Nuphar lutea	Common	Yellow Water-lilly	Alcohol, "Brandy bottle".
Cretonia dalea	Jamaica	Leaves	Cigars.

Preparation of Perfumes.

An **Essence** is a solution of one pure essential oil in alcohol, usually of about 5 per cent strength. In France, and frequently elsewhere, the term "essence" is understood to refer to the oil or basic substance itself. In the flavoring extract industry the word us usually held to be synonymous with the term "extract" or "flavor."

An **Extract**, "extrait" or "perfume" is a blend of various raw materials with fixitives dissolved in alcohol, frequently to the extent of about 5 per cent. "Fluid extracts" contain glycerine.

A **Water**, "eau" or "aqua" is a solution of very small amount of essential oil in water, generally not over two parts per thousand. Talc is often used to put the oil more readily into solution.

In perfumery the term alcohol always means "Cologne Spirits" which is pure ethyl alcohol of about 95 per cent, and costs about $2.50 per gallon. For laboratory work "Columbian Spirits" which is pure methyl alcohol of about 95 per cent may be used. This is much less expensive, costing about $1.00 per gallon, and seems to be just as good.

The following are among the more popular perfumes. Extracts are made from the oils as described above.

Superfine Cologne Oil.

Bergamot oil,	2.50 drams.
Lemon oil,	6.00 "
Neroli Bigarde,	4.75 "
Rosemary oil,	2.50

Finest Florida Oil.

Bergamot oil,	2.25 drams.
Lemon oil,	4.00 "
Lavender oil,	0.50 "
Clove oil,	0.25 "

Hovenia Oil.

Lemon Oil	1.50 drams.
Neroli Bigarade	10.00 minims.
Rose Oil	10.00 minims.
Clove Oil	7.00 minims.

Huile Japonaise.

Sandalwood Oil	1.50 drams.
Patchouli Oil	1.00 dram.
Verbena Oil	1.00 dram.
Cedarwood Oil	1.00 dram.
Neroli Bigarade	0.25 dram.

Extrait de Chypre.

Essence of Rose	2 drams.
Tr. Ambergris	1 dram.
Tr. Musk	1 dram.
Tr. Coumarin(1)	1 dram.
Tr. Vanilla(2)	1 dram.
Tr. Orris Concrete(1)	1 dram.

(1 = 20 p.c., 2 = 40 p.c., tincture.)

Extract of Tea Rose.

Essence of Rose	2.00 drams.
Essence of Geranium	1.00 dram.
Essence Neroli Bigarade	0.25 dram.
Essence of Sandalwood	0.25 dram.
Tr. Orris Concrete	0.25 dram.

Extract of Mignonette.

Neroli Bigarade Oil	10.00 minims.
Rose Oil	10.00 minims.
Bergamot Oil	15.00 minims.
Tr. Orris Root	8.00 drams.
Tr. Coumarin	1.00 dram.
Tr.Nettle Herb(1)	1.00 dram.
Tr. Storax(2)	0.50 dram.
Tr. Ambergris	15.00 minims.
Tr. Musk	10.00 minims.
Benzaldehyde	2 drops.

(1 = extract 48 hrs.with 4 parts warm alcohol, 2 = extract with 5 parts warm alcohol and filter.)

Extract of Heliotrope.

Essence of Rose	6.5 drams.
Essence Neroli Bigarade	1.5 drams.
Tr. Ambergris	1.0 dram.
Tr. Vanillin	13.0 drams
Benzaldehyde	0.25 dram.

Lavender Water.

Oil of Lavender	2.00 c.c.
Talc (purified)	15.00 grams.
Water (distilled)	to 1000 c.c.

Fluid Extract of Red Rose.
(by percolation)

Red Rose Leaves (course powder)	1000 grams
Alcohol (80 p.c.)	900 c.c.
Glycerine	100 c.c.

PART II.

Experimental.

A. Physical Analysis:

1. Specific gravity (D.) use a 25 cc., or a 10 cc., specific gravity bottle (pyknometer) preferably one with thermometer attached. Weigh it at 15° C. (room temperature), fill with oil, allow to stand in a water bath of 15° C. for 20 minutes. Remove, dry, put stopper in quickly to eliminate bubbles, wipe off any drops of oil on the point of the escape tube, put on the escape tube cap and weigh. The difference is the weight of 25 cc. which divided by the weight of water which the bottle holds at 15° C. gives D.

D may also be determined accurately and quickly by means of a Westphall balance.

If less than 10 cc. of oil is at hand pipett out 5 cc. with a 5 cc. straight pipett, and transfer to a No. 00 tared beaker. Allow to drain five minutes, and finally blow out the last drop, blowing through a $CaCl_2$ drying tube. Weigh and divide by 5. This method is approximate.

D. correction: .0005 less for each degree above 15° C.

2. Specific refractive index ($n_{D_{20}}$). Taken directly with a Zeiss-abbe refractometer. A water-jacketed one is best.

$n_{D_{20}}$ correction: .000365 less for each degree above 20° C.

3. Specific rotation (a_d). Observe, by means of a Laurent half-shadow polariscope, the "observed" rotation and divide by D. If this instrument is not available a saccharimeter may be used.

1 per cent = 1° Ventzke (Sugar-Vernier scale) ≡ .3455° Rotation (Na.light)
≡ .3906° Rotation (white light)

Essential oils are always observed through a 100 mm. tube, except certain dark oils, e.g., bergamot, which requires a 50 mm. tube.

Do not forget to divide the observed rotation by D. in order to obtain a_d which is the standard.

If only a very small amount of oil is at hand weigh out exactly 1 gram, and dissolve it in 10 cc. of absolute alcohol. The difference between the rotation of the absolute alcohol and that of this mixture gives .1 of the observed rotation of the oil.

4. Solubility. Shake one volume of the oil with 1.2 and 3 volumes respectively of 70, 80, and 90 per cent alcohol. The point at which the greatest amount of oil is dissolved to a clear solution in the least amount of alcohol is the solubility.

5. Fractional distillation and observation of the temperatures and physical properties of the fractions in one of the simplest and best ways of making an approximate analysis as it immediately reveals, in most cases, the existence of adulteration. Use a fractionating flask together with either a Brühl or a Fischer and Harries receiver if it is to be distilled at reduced pressure. A standard manometer is best, but a serviceable pressure gauge may be constructed as follows:

Select a small sized, rather thick, piece of glass tubing, about 5 feet long, and bend as shown in the digram. Clean the tube with chromic acid mixture and dry. Glass stopcocks and pressure tubing form the connections. A piece of millimeter plotting paper makes a convenient scale on which to mark off 760 mm. Tack the bent tubing onto a long board on which has been glued the scale, and fill it to 380 mm. with Hg. When completed the reduced pressure apparatus will look as shown in Fig. 2.

B. Chemical Analysis.

1. Detection and estimation of free acids. ("Acidity" or "Acid Value"). Acidity is the number of KOH necessary to neutralize the free acid in 1 gram of oil.

Angelica, Cypress, Orris-root and Saffron are types of oils of considerable free acid content.

Dissolve a known weight of the oil (2 grams) in neutral methyl alcohol, add a few drops of phenolphthalein and titrate with $\frac{n}{2}$ NaOH.

1 cc. $\frac{n}{2}$ NaOH = .030 gms. acetic acid
= .051 gms. valeric acid.

2a. Detection of phenols. Thyme, Clove, Sassafras and Anise are types of oils rich in phenols.

Chapman's test:---Dissolve 1 cc. of the oil in 5 cc. of acetic anhydride and add 1 to 2 trops conc. H_2SO_4.

Eugenol: Brown,→purple,→wine-red.
Iso-eugenol: Rose-red,→light brown.
Safrol: Emerald-green,→brownish-green,→brownish.
Iso-safrol: Pale pink,→reddish.
Estragol: Purple,→indigo-blue,→bluish-purple.
Anethol: Pale yellow after one-half hour.
Other phenols: Violet with $FeCl_3$ (conc.)

2b. Estimation of phenols. Into a 150 cc. Hirschsohn flask (has a narrow neck graduated to 10 cc. in tenths), measure out exactly 10 cc. of the oil, add a convenient quantity of 5 per cent NaOH and shake 10 to 15 minutes. Allow to stand until the oil has separated, add water carefully bringing the oil up into the neck, and read off the deficiency (equals per cent phenols), If the oily and aqueous layers do not separate, add a definite volume of petroleum ether and subtract from result.

For very small quantities, measure out exactly 2 cc. into a 40 cc., 10 per cent milk-fat bottle with the neck holding 2 cc. graduated in tenths. Follow foregoing directions. After absorbtion read off per cent of phenols direct.

3a. Detection of aromatic alcohols (monatomic). Sandalwood, Geranium, Peppermint and Rose are types of oils rich in free alcohols.

Bitto's test:---Shake 5 cc. of the oil with 2 cc. of a solution of methyl violet (.5 g. to 1 liter of water) + 1 cc. K_2S solution. If an alcohol is present a cherry-red to violet color appears. If none, the mixture becomes greenish-blue, precipitates reddish flocks and finally appears yellow.

3b. Estimation of aromatic alcohols.

(A) Oils ester free or of negligible ester content. The alcohols in the oil are converted into the acetic esters as follows:

Ten to 20 cc. of the oil are mixed with an equal volume of acetic anhydride and about 2 grams anhydrous sodium acetate ($NaC_2H_3O_2$) to absorb the water liberated. Boil under a reflux 2 hours. Cool and shake with 2 volumes of water. Repeat until the water shows a neutral, or at least faintly acid reaction. Dry the acetylated oil over anhydrous potassium acid sulphate ($KHSO_4$) and, if necessary, filter. A known weight (2 to 5 grams) of the acetylated oil is now saponified by a solution of $\frac{n}{2}$ KOH in alcohol (15 to 25 cc) by boiling briskly under a reflux for one-half hour. The amount of alkali used is determined as usual by titration with $\frac{n}{2}$ HCl.

N.B. In case citronellal, terpineol or linalol are present in the oil dilute the oil with five times its weight of pure turpentine and acetylate with eight times its weight of acetic anhydride. Run duplicate blanks and make the proper deduction. Calculate the per cent of free alcohols in terms of the predominating one as follows:

$$P = \text{per cent} = \frac{\frac{m}{2} \times N}{10(W - .042N)}$$

$\frac{m}{2}$ = one-half molecular weight of the alcohol present.

N = No. cc. $\frac{n}{2}$ KOH used in its ester saponification.

$.042\,N$ = Correction for increase in weight due to acetylation.

W = Weight of oil saponified.

(B) Oils of considerable ester content.

1. Estimate the combined alcohols (ester value, Q.V.)

2. Saponify 20 grams of the oil with calculated amount of KOH in alcohol as usual. Wash the ester-free oil well, and dry over anhydrous potassium acid sulphate ($KHSO_4$).

3. Estimate total alcohol in 2 to 5 grams of the ester-free oil as in A.

4. Deduct the amount of combined alcohols from the amount of total alcohols which gives the amount of free alcohols.

Detection and estimation of esters (ester value).

Lavender, Bergamot, Chamomile and Wintergreen are typse of oils rich in esters. The ester value is the number of milligrams of KOH necessary to saponify the esters in 1 gram of the oil.

N.B. The Saponification Number is the ester value plus the acid value. Therefore, when there is no acid value the S.N. is the ester value.

S.N. = 15 ≡ 1.5 per cent KOH

S.N. ---- per cent ester; see p. 119 Parry.

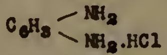
Saponify in duplicate 2 to 5 grams of the oil by boiling with 25 cc. $\frac{n}{2}$ KOH in alcohol under a refulx for one-half hour; and titrate the excess of alkali with $\frac{n}{2}$ HCl.

Calculate per cent of esters in terms of predominating ester.

1 cc. $\frac{n}{2}$ KOH = .118 g. geranyltiglate ($CH_3.CH:C(CH_3)COOC_{10}H_{17}$)

= .086 g. linalylacetate ($CH_3COOC_{10}H_{17}$)

5a. Detection of aldehydes and ketones. Lemon-grass, Citronella, Cinnamon and bitter almond are types of oils rich in aldehydes. Spearmint, Pennyroyal and Sage are types of oils rich in ketones.

Aldehydes and ketones frequently occur together. Both will produce a fine greenish fluorescence in 10 to 15 minutes on adding to 2 cc. of oil 5 cc. of an alcoholic solution (.5 to 1 per cent) of a meta diamino-salt, e.g., diamino-benzene-hydrochloride  $C_6H_3 \begin{matrix} \diagup NH_2 \\ \diagdown NH_2.HCl \end{matrix}$ slightly acidified. If the test is positive, make Schiff's test to which aldehydes only respond. Shake 2 cc. of the oil in absolute alcohol with 1 cc. Schiff's reagent. Intense purple-red color. If this test is negative and the first is positive, ketones are present.

Schiff's reagent:---Dissolve 1 gram fuchsine in 1 liter H_2O and add 20 cc. of sodium acid sulphite ($NaHSO_3$) solution (30° Bé.) + 10 cc. conc HCl.

5b. Estimation of aldehydes and ketones. Remove free acids by shaking with Na_2CO_3, and esters by hydrolyzing with NaOH before estimating as they would render the results unreliable.

Into a 150 cc. Hirschsohn flask measure out exactly 10 cc. of the oil. Add enough hot 40 per cent solution of sodium acid sulphite ($NaHSO_3$) to one-third fill the flask. Shake into the neck. Add 50 cc. more of the acid sulphite solution and shake and heat on steam bath until the clear oily layer floats on the surface. Allow to stand four hours. Shake, add more of the solution until the oily layer is forced up into the neck. Read off the deficiency (= per cent aldehydes and ketones).

N.B. Not applicable to citral unless in large quantities(e.g. lemon-grass oil). For very small quantities use the 10 per cent milk-fat bottle, as under phenols, following above directions.

6. Detection of water. Mix 10 cc. of the oil with 40 cc. petroleum ether. Water separates in minute globules which coalesce and sink to the bottom. There should not be more than a drop or so.

7. Detection of alcohol, C_2H_5OH. Gradually add some dehydrated calcium chloride ($CaCl_2$) to the anhydrous oil while shaking and heating on the water bath. Mere traces of alcohol render the first portions of calcium chloride

pasty, but if present in larger proportions the salt dissolves forming a heavy liquid layer.

8. Detection of turpentine. Dissolve 20 grams potassium acid tartrate ($KHC_4H_4O_6$) plus 6 grams manganese carbonate ($MnCO_3$) in 1 liter of water. Add 3 cc. of this solution plus 5 drops NH_4OH to 5 cc. of the suspected oil. Shake, heat on water bath, and while heating, pass a current of air through it. Oils of lemon ahd bergamot turn brownish. Oil of turpentine turns intense brownish black. All other oils, a faint yellow.

9. Burgess' test. Dissolve 10 grams mercuric sulphate ($HgSO_4$) in 25 per cent H_2SO_4 to form 100 cc. of solution. Vigorously shake 2 cc. of the oil with 5 cc. of this reagent and note color after 10 minutes.

Citral: bright red--> whitish.
Citronella: bright yellow.
Limoneve: evanescent flesh color.
Linalylacetate: bright violet.
Linalol: deep purple.
Caryophyllene: yellowish.

10. Sesqui-terpene test. Dissolve 1 to 2 cc of the oil in 5 to 6 cc. of glacial acetic acid, and add 3 to 4 drops of conc. H_2SO_4. Green--> blue--> red.

11. Detection of stearoptenes. To 5 cc. of the oil add 10 cc. of 85 per cent alcohol, and allow to stand over night. The naturally occuring paraffin rises to the top while fatty oils or other adulterants settle out.

GERANIUM OIL (Oleum Geranii)

1. Botanical derivation: Pelargonium odoratissimum.

   a. Habitat: South France, Spain, Rèunion, Algeria.

   b. Extraction: Distillation of green parts of plant only.

   c. Per cent yield: .15 to .33 per cent.

2. Physical properties:

   D_{15} = .888-.906

   $n_{d_{20}}$ = 1.4650

   a_{d} = -6° to -16°

   Color: greenish to brownish.

   Sol. 1 - 3 of 70 per cent alcohol.

3. Constituents:

Geraniol,	60 - 70 per cent
Citronellol,	15 - 35 " "
#Esters,	15 - 25 " "
Stearoptene L.Menthone Blue high boiling fraction	5 - 3 " "
Pinene Phellandrene Linalol Amyl alcohol	(Traces)

#Mostly as geranyl tiglate.

4. Adulterants:

   a. Benzoic acid esters (cause high "ester value")

   b. Indian geranium oil (raises $n_{d_{20}}$)

   c. Turpentine (decreases sol.)

   d. Cedar-wood oil (decreases sol.)

   e. Fatty oils (residue on evaporation)

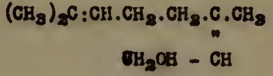
5. Chemical Analysis: Follow general outline of analysis, omitting B2a and b, and 5b, and including the special directions given below. Verify the results with those given either in this book or in others.

a. Chemistry of geraniol, $C_{10}H_{17}OH$.

Synonyms: Rhodinol, Lemonol.

Definition: Monatomic primary olefinic terpene alcohol.

Formula:



$$(CH_3)_2C{:}CH.CH_2.CH_2.\underset{\underset{CH_2OH\ -\ CH}{\|}}{C}.CH_3$$

Chief Occurrence: Palmarosa, rosa, geranium.

Detection: Two drops of oil, plus 5 cc. alcohol, plus 10 drops conc. H_2SO_4 without shaking. Acid is intense orange-yellow. Neutral zone is durable reddish-violet.

Physical Properties:

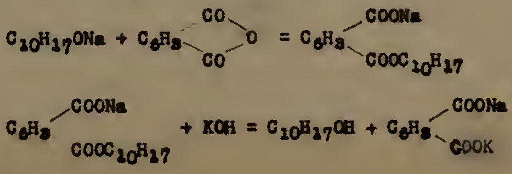
D_{15} = .8801 Color: colorless.

$n_{d_{20}}$ = 1.4780 Sol. 1 - 1 (95 per cent alcohol)

a_d = inactive B.P. 230°

Isolation and estimation: To separate in a state of absolute purity. Take an amount of anhydrous geranium oil (50 grams) containing a known weight of geraniol. Add a corresponding weight of metallic sodium. Treat the sodium geraniolate with ether plus a calculated amount of phthalic anhydride. Boil on water bath under reflux for one hour. Hydrolyze the sodium geraniol phthalate with calculated amount of KOH in alcohol under a reflux one hour. Cool by adding water. Separate, dry over anhydrous $KHSO_4$ and weigh.

Reactions: $2C_{10}H_{17}OH + 2Na = 2C_{10}H_{17}ONa + H_2$



$$C_{10}H_{17}ONa + C_6H_4\begin{matrix}CO\\ \\ CO\end{matrix}\!\!>O = C_6H_4\begin{matrix}COONa\\ \\ COOC_{10}H_{17}\end{matrix}$$

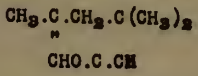
$$C_6H_4\begin{matrix}COONa\\ \\ COOC_{10}H_{17}\end{matrix} + KOH = C_{10}H_{17}OH + C_6H_4\begin{matrix}COONa\\ \\ COOK\end{matrix}$$

Transformation: Geraniol --> (1) a-citral --> (2) a-ionone.

(1) a-citral, C$_9$H$_{15}$CHO.

Synonyms: Geranaldehyde, geranial.

Formula:



$$\begin{array}{l} \mathrm{CH_3.\overset{}{C}.CH_2.C(CH_3)_2} \\ \quad\;\; '' \\ \quad\mathrm{CHO.C.CH} \end{array}$$

Chief Occurrence: Lemon-grass, lemon, backhousia.

Detection: Burgess' test (Q.V.)

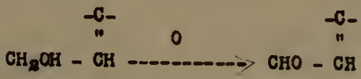
Physical Properties:

D_{15} = .8898 Collor: yellow.

$n_{d_{20}}$ = 1.4891 B.Pt. 228°

a_d = inactive

Formation: By careful oxidation with chromic acid.



$$\mathrm{CH_2OH - \underset{}{\overset{-C-}{\overset{''}{CH}}}} \xrightarrow{O} \mathrm{CHO - \overset{-C-}{\overset{''}{CH}}}$$

Dissolve 16 grams potassium dichromate ($K_2Cr_2O_7$) in 19 grams conc., c.p. H_2SO_4 in 150 cc. water. Twenty-two grams geraniol are added to the well cooled mixture. After nearly all the geraniol is added allow the mixture to warm up. Shake well a half hour. Now render slightly alkaline, and distil with steam. Separate the pure citral and dry over anhydrous potassium sulphate ($KHSO_4$). Good yield.

Important reaction: Mix 2 parts citral in a dry test tube with 1 part anhydrous $KHSO_4$. Heat to 170° for 20 minutes. Cymene ($C_{10}H_{14}$) results, which is the basis of very many constituents of essential oils.

Identification derivatives: (1) a-citral oxime, $C_{10}H_{16}NOH$. Formed by the action of 1.35 g. of hydroxyl amine hydrochloride, $NH_2OH.HCl$, plus .8 g. NaOH on an alcoholic solution of 3 grams citral. A yellowish-red oil.

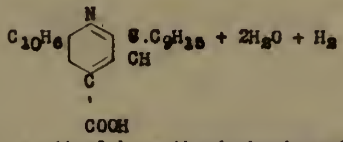
$$C_{10}H_{16}O + NH_2OH.HCl + NaOH \longrightarrow C_{10}H_{16}NOH + 2H_2O + NaCl$$

B.Pt. 143° at 12mm. $n_{d_{20}}$ -- 1.5143

SG. .9380

(2) a-citral b-napthocinchonic acid, $C_{23}H_{23}NO_2$. Mix 2 grams citral in alcohol with 2 grams pyroracemic acid and 2 grams of b-napthylamine[1]. Boil on water bath 2 hours. Cool, filter, purify by washing with ether. It recrystallizes from dilute alcohol in lemon-yellow leaflets which contain one-half molecule of H_2O, and melt at 197°. Yield: 1.4 grams. Very characteristic, and well adapted for detection of small amounts of citral.

Reactions: $C_9H_{15}CHO + CH_3COCOOH + C_{10}H_7NH_2 =$



a-citral-b-napthocinchonic acid.

(3) a-citral semicarbazone, $C_9H_{16}CON.NHCONH_2$. To one gram citral add 25 cc. semicarbazide solution[2]. Semicarbazone crystallizes out in 24 hours. Filter and precipitate remainder by adding water to filtrate. Purify by recrystallizing from methyl alcohol. M.Pt. 164°.

Reaction: $C_{10}H_{16}O + NH_2NHCONH_2 \dashrightarrow C_9H_{16}CON.NHCONH_2$

---

[1] B-napthyl amine, $C_{10}H_7NH_2$. Heat 30 grams b-napthol with calculated amount of chlor-zinc ammonia (calculate amount of dry stick $ZnCl_2$ dissolve in excess conc. NH_4OH) under slight pressure (780-790 mm.) for 2 to 3 hours to 180 to 200° C. Pour while hot the supernatant liquid into a large folded filter Do not allow the resinous residue to accompany it. Boil to one-half volume, and refilter if necessary. Allow to cool when b-napthyl amine separates in small pearly plates. M.Pt. 111°.

$$C_{10}H_7OH + NH_3 \dashrightarrow C_{10}H_7NH_2 + HOH$$

Pyroracemic acid, $CH_3CO.COOH$. Take 25 grams tartaric acid and dry it with an equal weight of powdered anhydrous $KHSO_4$. Dense white fumes of CO_2 , and at rather below 165°, liquid pyroracemic acid distils over. Catch all above 125° and redistil to free from fumes. B.Pt. 165° C.

$$\underset{\text{Tartaric acid}}{COOH.CHOH.CHOH.COOH} \dashrightarrow \underset{\text{Glyceric acid}}{CH_2OH.CHOH.COOH} + CO_2$$

$$\underset{\text{Glyceric acid}}{CH_2OH.CHOH.COOH} \dashrightarrow \underset{\text{Pyroracemic acid}}{CH_3CO.COOH} + H_2O$$

[2] Semicarbazide, $NH_2NHCONH_2$. Dissolve together 13 grams hydrazine sulphate, $N_2H_4H_2SO_4$, plus 5.5 grams Na_2CO_3, plus 4 grams KCN in 100 cc water. M.Pt. 96° Reduces Fehling's solution in cold.

2. (Continued) Hydrazine sulphate, $N_2H_4H_2SO_4$. Mix 200 cc. of a solution of 7.5 grams NaOCl in a flask. Boil one-half hour. Cool, place flask in ice water and add 20 cc. of a splution 1.96 grams H_2SO_4. Hydrazine sulphate crystallizes out. Recrystallize from water.

$$NH_2Cl + NH_3 \dashrightarrow N_2H_4.HCl$$
$$2N_2H_4.HCl + H_2SO_4 \dashrightarrow 2N_2H_4.H_2SO_4 + 2HCl$$

J. W. Mellor, Mod. Inorg. Chem.

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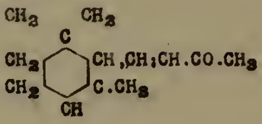
(2) a-ionone, $C_{13}H_{20}O$.

Synonym: Artificial violet.

Formula:



Physical properties:

D = .9350 B.Pt. 135° at 17 mm.

$n_{d_{20}} = 1.5070$

Formation: Mix together 10 grams citral, plus 10 grams acetone, plus 25 cc. of strong solution of barium hydroxide ($Ba(OH)_2$). Shake as constantly as possible for 2 to 3 days. Dissolve the products of the reaction in ether. Distil off the ether and then continue to distil with steam which volatilizes the unsued acetone, citral and volatile products of the condensation of acetone. The product of condensation remaining as a residue is separated and dried over anhydrous $KHSO_4$. It is pseudo-ionone, $C_{13}H_{20}O$.

Take 20 parts crude pseudo-ionone plus 100 cc. of a solution of 2.5 grams H_2SO_4, plus 100 parts glycerine and heat to boiling on an oil bath under a reflux for 2 hours. Dissolve the product in ether. Separate ethereal solution and distil off ether. Continue at 17 mm. pressure collecting fraction 133 to 140°. Purify this by converting it with phenyl-hydrazine into a ketone condensation product which under the action of dilute HCl decomposes wholly into a-ionone.

Reaction: $C_{10}H_{16} + CH_3COCH_3 \dashrightarrow C_{13}H_{20}O + H_2O$

$$\underset{\text{Pseudo-ionone}}{C_{13}H_{20}O}\text{, molecular rearrangement} \dashrightarrow \underset{\text{Ionone}}{C_{13}H_{20}O}$$

For favorable results careful manipulation is essential. By using conc. H_2SO_4 b-ionone is produced.

"Triple extract of violets" is prepared by dissolving one gram of a- or b-ionone or a mixture of each, to suit taste, in one liter of cologne spirits, which is pure odorless ethyl alcohol.

CLOVE OIL (Oleum Caryophyllorum)

1. Botanical derivation: Eugenia caryophyllata.

   a. Habitat: Zanzibar, Madagascar, Réunion.

   b. Extraction: Distillation of buds and stems.

   c. Per cent yield: 15.0 to 18.0 per cent.

2. Physical properties:

   $D_{15} = 1.050$ Color: Light brownish-yellow.

   $n_{d_{20}} = 1.5280$ Sol.: 1 - 2 of 70 per cent alcohol.

   $a_d = 0^\circ$ to -1° B.Pt.: 245° C .

3. Constituents:

Eugenol,	80 - 95 per cent
Eugenylacetate,	7 - 17 " "
Caryophyllene	5 - 20 " "

Heptyl-methyl-ketone)
Vanillin) (Traces)
Furfurol)
Naphthaline)

4. Adulterants.

   a. Oil of Clove stems giving a coarser odor.

   b. Cedar-wood oil, lowering "D" and raising "a_d".

   c. Turpentine, lowering solubility.

   d. Petroleum, lowering solubility.

   e. Ethyl alcohol, lowering both "D" and B.Pt.

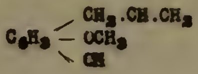
Chemical Analysis: Follow the general outline, omitting B, 3b and 5b, and including the special directions given below, verifying all results.

Constituents: (A) Eugenol, $C_{10}H_{12}O_2$.

Synonym: Allyl Guaiacol.

Definition: a-methoxy-allyl-phenol.

Formula:



$$C_6H_3 \begin{matrix} / \; CH_2.CH.CH_2 \\ - \; OCH_3 \\ \backslash \; OH \end{matrix}$$

Chief Occurrence: Acacia, Bay, Cinnamon, Clove.

Detection: Chapman's test (Q.V.)

Physical Properties:

D_{15} = 1.070

$n_{d_{20}}$ = 1.5400

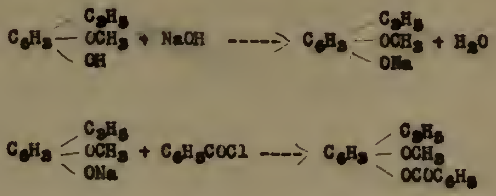
Color: Light brown.

Sol.: 1 - 2 of 70 per cent alcohol.

B.Pt.: 253° C.

Estimation, (After Thoms): In a tared 150 cc. beaker, 5 grams of the oil are treated with 20 cc. of 15 per cent NaOH plus 6 grams of benzoyl chloride. Stir well. The sodium eugenate first solidifies and then dissolves. Heat fifteen minutes on a water bath. After cooling, 50 cc. of water are added and the crystalline ester is heated until it has again become oily and then cool. Decant the supernatant liquor. Repeat three times to free from caustic soda and other impurities. Transfer carefully all the crystals of benzoyl-eugenol, still moist, to a beaker and treat with 25 cc. of 90 per cent alcohol. Heat with agitation until dissolved,now cool until crystallization is complete. Transfer the precipitate to a 9 cm. tared filter paper and collect the filtrate in a graduate. About 20 cc. should be obtained. The alcoholic solution held in the crystalline mass is forced out by adding 90 per cent alcohol until the filtrate measures 25 cc. The still moist filter with its precipitate is transferred to a weighing tube, dried at 100° C. and weighed. Benzoyl eugenol is dissolved to the extent of .55 grams by 25 cc. of 90 per cent alcohol which amount is added to the final weight. M.Pt. 50° C.

Reactions:



$$C_6H_3\begin{cases}C_3H_5\\OCH_3\\OH\end{cases} + NaOH \dashrightarrow C_6H_3\begin{cases}C_3H_5\\OCH_3\\ONa\end{cases} + H_2O$$

$$C_6H_3\begin{cases}C_3H_5\\OCH_3\\ONa\end{cases} + C_6H_5COCl \dashrightarrow C_6H_3\begin{cases}C_3H_5\\OCH_3\\OCOC_6H_5\end{cases}$$

$$X = \frac{4100(a + .55)}{67 \times b}$$

X = Per cent of eugenol.

a = Weight of benzoyl-eugenol.

b = Weight of clove oil used.

a + .55 = Correction.

Isolation: Agitate 45 cc. of clove oil plus 135 cc. of ether with 150 cc. of 10 per cent caustic potash in a separatory funnel. The ethereal liquid contains the caryophyllene. Separate the potassium eugenate solution and acidify with dilute hydrochloric acid. Wash the liberated eugenol with water, and dry over anhydrous potassium acid sulphate.

Transformation: Eugenol to vanillin.

Vanillin, $C_8H_8O_3$.

Synonym: Synthetic Vanilla.

(1) Botanical Derivation: Vanilla Planifolia.

a. Habitat: Mexico, Java, Rèunion.

b. Extraction: "Curing" of pods and beans.

c. Per cent yield: 1.1 - 2.9 per cent.

(2) Physical Properties:

White needles, subliming at 150° C.

M.Pt.: 80° Sol.: 1 - 90 of water

B.Pt.: 285° in CO_2 " 1 - 1 of 90 per cent alcohol.

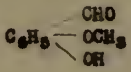
(3) Adulterants:

a. Benzoic acid, detected by adding sodium carbonate, filtering and precipitating ferric benzoate.

b. Acetanilide detected by boiling with potassium hydrate and testing for aniline.

(4) Definition: Methoxy-protocatechnic aldehyde.

Formula:



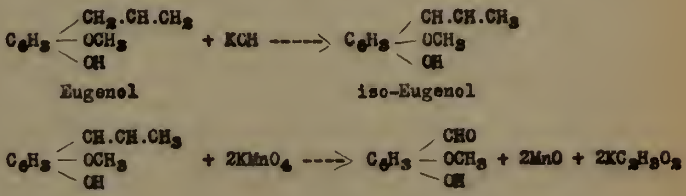
$$C_6H_3 \begin{cases} CHO \\ OCH_3 \\ OH \end{cases}$$

(5) Detection: Schiff's test, (Q.V.)

(6) Formation: The best yield is obtained by first converting the eugenol (30 cc.) into iso-eugenol by treating it with a calculated amount of potassium hydrate in alcohol, and boiling under a reflux twenty minutes. Add water enough to throw the product out of solution, separate and wash until only slightly alkaline. Now take 25 cc. of iso-eugenol, add 30 cc. of acetic anhydride plus 3 grams of sodium acetate and boil under a reflux for two hours. Cool and shake with two volumes of water in a separatory funnel.

All of the acetic eugenol obtained is dissolved in 25 cc. of glacial acetic acid plus 75 cc. of water and oxidized with a calculated amount of finely ground potassium permanganate which is slowly added to the warm solution with great care, and constant agitation. During the violent reaction a voluminous precipitate of manganous oxide separates. After the reaction has subsided, filter off this precipitate on a Witt filter. Render the filtrate slightly alkaline and extract with violent shaking in a separatory funnel with three lots of ether of 50 cc. each, and allow the ether to evaporate off at room temperature after having dried the ethereal solution thoroughly over anhydrous potassium acid sulphate. The crude brownish crystals of vanillin may be redissolved in 25 cc. of ether and purified by extracting with a concentrated solution of sodium acid sulphite which forms the usual addition product. This is filtered off, washed with ether and decomposed with dilute sulphuric acid and the pure vanillin extracted with ether from which solvent it is obtained in fine white crystals.

Reactions:



$$C_6H_3\begin{array}{l}\diagup CH_2.CH.CH_2\\ - OCH_3\\ \diagdown OH\end{array} + KOH \dashrightarrow C_6H_3\begin{array}{l}\diagup CH.CH.CH_3\\ - OCH_3\\ \diagdown OH\end{array}$$

Eugenol iso-Eugenol

$$C_6H_3\begin{array}{l}\diagup CH.CH.CH_3\\ - OCH_3\\ \diagdown OH\end{array} + 2KMnO_4 \dashrightarrow C_6H_3\begin{array}{l}\diagup CHO\\ - OCH_3\\ \diagdown OH\end{array} + 2MnO + 2KC_2H_3O_2$$

(7) Standard vanillin preparations in use by confectionery and chocolate factories.

(a) Two and five tenths vanillin sugar. To 25 grams of vanillin is added 100 grams of absolute alcohol plus 975 grams of pulverized sugar. Evaporate the alcohol off in a warm place and then pulverize and sift the sugar which keeps its odor indefinitely and is equal to that of the finest natural vanilla.

(b) Two and five tenths per cent essence of vanillin. Crystallized vanillin, 25 grams in amount, is dissolved in 490 grams of absolute alcohol, and 485 cc. of distilled water. This is equal in strength to the finest vanilla essence.

(B) Caryophyllene, $C_{15}H_{24}$.

Synonym: Artificial Carnation.

Definition: A sesqui-terpene.

Occurrence: Clove and Copaiba.

Dection: Sesqui-terpene test (Q.V.)

Isolation and Approximate Estimation: Saponify 50 grams of clove oil with 200 cc. of 15 per cent caustic soda by heating on water bath under a reflux for half an hour. Separate the supernatant caryophyllene from the sodium eugenate solution, and wash it twice with caustic soda solution and several times with water. Carefully separate the caryophyllene, running it into a tared, three-inch crystallization dish. Allow to stand twenty-four hours in a desiccator and weigh. Repeat to constant weight.

Physical Properties:

D_{15} = .908 a_d = -9^0

n_d = 1.5009 B.Pt. = 258° C.

Identification Derivative: To 10 cc. of caryophyllene add 10 cc. of petroleum ether and 10 cc. of a saturated solution of sodium nitrite. Now add acetic acid slowly, shake well and freeze for two hours. Caryophyllene nitrosite, $C_{15}H_{24}N_2O_3$, will separate in a solid mass of blue needles. M.Pt. 113°.

TURPENTINE OIL (Oleum Terebinthinae)

1. Botanical derivation: N.O. coniferae (Pinus, Picea and Abies)

   a. Habitat: Europe and North America.

   b. Extraction: By steam, distillation of the oleo-resins and destructive distillation of the wood.

   c. Per cent yield: 10 - 25 per cent.

2. Physical properties:

D_{15} = .855 - .875

$n_{d_{20}}$ = 1.4667 - 1.4722

a_d = -34° to +29°
-2° to +14° Av.

Acidity: 108 - 145

Ester Value: 3 - 60
10 - 33 Av.

Color: Water-white.

Sol.: (Fresh) 1 - 6 of 90 per cent alcohol

Sol.: (Old) 1 - 3 of 90 per cent alcohol

B.Pt. 155° - 185° (95 per cent)

Iodine number: 310 - 350 per cent in 20 minutes.

Flash point: 33.3° C.

Saponification number: 140 - 161

3. Constituents:

American Turpentine (From Pinus Australis, i.e., Georgia yellow pine)

Pinene,	80 - 95 per cent
Dipentene,	5 - 10 " "
Fixed residue,	1 - 2 " "

Russian Turpentine (From Pinus Sylvestris)

Sylvestrene,	60 - 70 per cent
Pinene,	30 - 35 " "
Fixed residue,	1 - 2 " "

Camphene)
Camphoraldehyde)
Fenchene) Traces in both
Formic acid)
Acetic acid)

4. Adulterants:

a. Petroleum; 1 per cent lowers Flash Point 12 degrees.
Shake with aniline when two layers form.

b. Resin Oils, having Iodine number:	272
c. Wood Spirits, " " "	212
d. Camphor Oil, " " "	136
e. Eucalyptus Oil " " "	116
f. Substitutes " " "	
I. "Canadian Turpentine"	172
II. "Terebo"	58
III. "Imported Spirits"	2.6
IV. "Blended Turpentine"	32
V. "South American"	121
VI. "Turpentine Substitute"	55
VII. "Beadless Solvent"	5
VIII. "Turpolene"	39
IX. "Patent Turpentine"	15

5. Chemical Analysis: Follow the general outline, omitting B2b, 3b, 4 and 5b, and including the special directions given below, verifying results.

Important Tests.

I. "Pure Turpentine" test: Reagents (a) Two per cent solution of the sample in 95 per cent pure alcohol. (b) A solution of 5 grams KBr plus 1.5 grams $KBrO_3$ in 100 cc. distilled water. (c) A solution of 20 cc. pure concentrated sulphuric acid in 60 cc. distilled water. Take equal parts of each and shake well one minute, keeping temperature at 20° C. Pure turpentine discolorizes the solution.

II. Detection of Rosin Spirit: Shake 10 cc. of sample with 20 cc. of a solution of sulphurous acid. A snow-white emulsion shows absence of Rosin Spirit.

III. Iodine Number; Reagents: (a) Decinormal thiosulphate. Use 24.6 grams of pure sodium thiosulphate to the liter. (b) Decinormal dichromate. Use 3.874 grams of pure potassium dichromate to the liter.

Standardization: take exactly 20 cc. $N/10\ K_2Cr_2O_7$ plus 10 cc. 15 per cent KI solution, plus 5 cc. of concentrated hydrochloric acid, and titrate with $N/10\ Na_2S_2O_3$ until colorless, using fresh starch indicator.

Reaction: $K_2Cr_2O_7 + 14HCl + 6KI = 2CrCl_3 + 8HCl + 6I + 7H_2O$

e.g. used: 16.4 cc. $N\ 10\ Na_2S_2O_3$

1 gram I_2 = 16.4 x 5 = 82 cc. $N\ 10\ Na_2S_2O_3$

$\therefore$ 1 cc. $N\ 10\ Na_2S_2O_3$ = .0122 grams I_2

In theory 1 cc. $N/10\ Na_2S_2O_3$ = .0127 grams I_2.

(c) The Wijs Iodine Solution (Leach, Food Analysis): Dissolve 4.5 grams pure iodine in 180 cc. glacial acetic acid, and pass through a larger portion of this solution a current of carefully washed and dried chlorine gas until the solution is barely decolorized. Finally add the balance of the original solution of iodine to restore the iodine color so that there is a slight excess of iodine.

(d) Starch Paste Indicator: To one liter of boiling water add 5 grams of starch which has been ground to a paste in a little cold water. Boil one minute. When cool add 5 grams of potassium iodide and three drops of clove oil as a preservative.

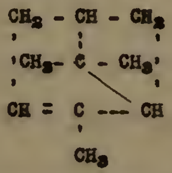
Procedure: Exactly .5 grams of the sample is weighed into a 50 cc. graduated flask which is then filled to the mark with chloroform. Run duplicate analyses and balnks. The solution being well mixed, 10 cc. is transferred to a 250 cc. glass stoppered bottle, and mixed with 30 cc. of Wijs solution which contains not less than .7 grams of iodine. Shake violently twenty minutes. After exactly twenty minutes an excess (10 cc.) of 15 per cent potassium iodide solution is added, and the solution titrated with N/10 thiosulphate until the brown iodine color is nearly gone, then add starch paste and continue until the blue color is discharged, shaking well at the end to get all the iodine out of the chloroform. There should be no return of blue color after five minutes. The difference between the amount of thiosulphate required for the blanke and the analyses shows the amount taken up by the unsaturated constituents of the oil in question. From this the per cent of iodine absorbed is readily calculated.

(A) Pinene, $C_{10}H_{16}$.

Synonyms: "Australene" in "d" form. "Terebenthene" in "L" form.

Definition: a Terpene.

Formula:



Chief Occurrence: Turpentine, cypress, laurel, valerian.

Detection: Mix 2 cc. of turpentine, plus 1 cc. concentrate hydrochloric acid, plus 1 cc concentrated ferric chloride. Color change: Rose ---> violet ---> red ---> blue.

Physical Properties:

D_{15} = .8604 Color: Water-white

$n_{d_{20}}$ = 1.4652 Sol.: 1 - 6 of 90 per cent alcohol.

α_d = +32° to -40° B.Pt.: 156.5° C.

Approximate Estimation and Isolation: Fractionally distil exactly 100 cc. of the oil, catching the fraction 153° to 158° in a tall 100 cc. graduate.[1]

Isolation: To isolate pure pinene, which is inactive, heat 10 grams of pinene nitrose chloride, as prepared below, for a short time with a mixture of 30 cc. of aniline and 80 cc. of 95 per cent alcohol under a reflux. After the violent action is over the product is steam distilled, and the aqueous distillate treated with an excess of acetic acid to remove the unchanged aniline. The hydrocarbon is then separated, washed again first with acetic acid then with water, dried over anhydrous potassium acid sulphate and distilled.

Reaction: $C_{10}H_{16}NOCl + 2C_6H_5NH_2 = C_6H_5N = NC_6H_4NH_2 + C_{10}H_{16} + HCl + H_2O$

Amino azo benzene   Pinene

Identification Derivative; Pinene nitrose-chloride, $C_{10}H_{16}NOCl$. to a mixture of 50 grams of turpentine, plus 50 grams of glacial acetic acid, plus 50 grams of ethyl nitrite,[2] well cooled by a freezing mixture, add gradually 15 cc. of concentrated hydrochloric acid. Pinene nitroso-chloride separates at once as a crystalline precipitate which is filtered by suction and washed by alcohol which precipitates out any of the product remaining in the filtrate. Combine the washed products, dissolve in chloroform and precipitate with methyl alcohol to further purify. M.Pt. 103° C.
With a molecular amount of aniline the chloride is transformed into Pinene nitroso-aniline. M.Pt. 125° C.

---

1. If the oil is resinous it must be first steam-distilled and thoroughly dried over anhydrous potassium acid sulphate.
2. Ethyl nitrite: To a solution of 200 grams of concentrated sulphuric acid in 1.5 liters of water add 100 grams of ethyl alcohol. Allow this mixture to flow into a solution of 250 grams of sodium nitrite in 1 liter of water, plus 100 grams of ethyl alcohol. The ethyl nitrite which forms at once must be condensed in well cooled recievers. Wallach.

(C) Transformation of Turpentine.

I. Turpentine to camphor; camphor, $C_8H_{14}COCH_2$

1. Botanical derivation: Laurus Camphora.

   a. Habitat: Formosa, Japan, Florida.

   b. Extraction: Sublimation from wood and twigs.[1]

   c. Per cent yield: Variable.

2. Physical Properties: It is a white, tough, easily subliming semi-crystalline mass of hexagonal stars.

D = .995

Sol. 1 - 1000 pts. water; complete in the solvents.

$a_d = \pm 44^{\circ}$

M.Pt. 175° Under pressure
B.Pt. 204°

3. Adulterants:

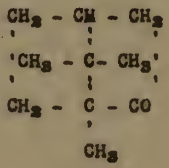
   a. Camphor Oil. Take M.Pt. and see Table p. 171, Allen.

   b. "Imitation Camphor": Pinene Hydrochloride.

   Boil a small amount with caustic potash and test for chlorides.

4. Definition: It is a cyclic ketone.

Formula:



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[1] Crude camphor oil:
(Light (camphor) oil, D = .910
(Heavy (sassafrassy) oil, D = .970
(Camphor D = .995

First the camphor is frozen out, then the light oil is distilled off and sold for making varnishes and soaps. The heavy oil of "Sassafrassy Camphor" is used to perfume soaps and as a solvent for resins and rubber. Its color is pale green, and its odor like sassafras, in fact 50 per cent of it is Safrol which is separated and used largely in the manufacture of heliotropin.

5. Detection: Ketone test (Q.V.)

6. Formation: Pass dry hydrochloric acid gas into 200 cc. of well dried turpentine, cooled by a freezing mixture, for two hours. Pinene hydrochloride (Iso-bornyl chloride, "Imitation Camphor") is thrown down as a crystalline mass. If rise in temperature is prevented the turpentine solidifies almost completely to a camphor-like mass upon becoming saturated with the hydrochloric acid gas. Separate the hydrochloride on a Witt filter and recrystallize from alcohol from which it is obtained in white feathery crystals.[1]

M.Pt. 125° "D" form is inactive.
B.Pt. 207° "L" form: -26.3°

To 50 grams of pinene hydrochloride, dissolved in a little alcohol, add a slight excess of strong ammonium hydrate, plus 5 grams of sodium acetate. Boil under a reflux fifteen minutes, and then heat in an open beaker until the excess of ammonia and alcohol is expelled. Upon cooling camphene crystallizes out. Pour off the supernatant ammonium chloride and wash the camphene with water. Recrystallize from 95 per cent alcohol when it separates in white feathery leaflets, much like camphor. M.Pt. 61°C., B.Pt. 160°

Heat 25 grams of camphene with molecular weights of potassium dichromate in sulphuric acid for a half hour on a water bath and then pour the whole into a large volume of cold water when camphor separates. Upon recrystallization from benzene it is obtained in white feathery needles.

---

[1] A copper wire dipped in a solution of the pinene hydrochloride gives a green flame test, while true camphor does not.

Reactions:

$$\underset{\text{Pinene}}{C_{10}H_{16}} + HCl \dashrightarrow \underset{\text{Pinene hydrochloride}}{C_{10}H_{17}Cl}$$

$$C_{10}H_{17}Cl + NH_4OH \dashrightarrow \underset{\text{Camphene}}{C_{10}H_{16}} + NH_4Cl + H_2O$$

$$C_{10}H_{16} + H_2CrO_4 \dashrightarrow \underset{\text{Camphor}}{C_{10}H_{16}O}$$

7. Estimation: (In celluloid, ivorine, xylonite, etc.) Saponify with 10 per cent caustic soda an amount of the sample containing 2 - 3 grams of camphor. Heat to 80°C until saponification is complete. Then add enough strong caustic soda solution to raise the strength of the liquid in the flask again to 10 per cent or slightly over. Dilute the contents to 250 cc. and distil to half volume. The condenser is connected air-tight to the receiver, a small Woulff bottle, whose second orifice is tightly connected with a U tube containing 20 cc. of carbon tetrachloride to catch any uncondensed camphor vapor. When the distillation is complete add the carbon tetrachloride to the contents of the receiver, and agitate to dissolve the camphor. Carefully separate this tetrachloride solution, make up with fresh tetrachloride to 25 cc. and take the polarimetric reading of 200 mm. at 20° C. Per cent camphor = $\frac{.22385\,a}{.95}$

8. Standard Pharmaceutical Preparations:

a. Camphor Water (1 per cent); one gram of camphor is dissolved in 3 grams of 90 per cent alcohol, and then made up to one liter with water.

b. Spirits of Camphor (10 per cent); 10 grams of camphor are dissolved in 90 grams of 90 per cent alcohol.

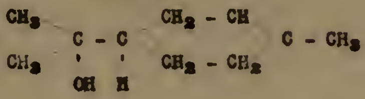
c. Camphor Liniment (21 per cent); 20 grams of camphor are dissolved in 80 grams of olive oil.

II. Turpentine to terpineol; terpineol, $C_{10}H_{17}OH$.

Synonym: "Artificial Lilac."

Definition: It is a terpene alcohol.

Formula:



Physical Properties:

D = .942 (Com'l liquid) M.Pt. 36° (Crystal. solid)

$n_{d_{20}} = 1.4747$ B.Pt. 217°

α_d = Inactive.

Formation: Mix 80 grams of turpentine in a flat basin with 20 grams of alcohol and 20 grams of nitric acid ($D = 1.25$). Allow to stand in a cool place for three days then neutralize with alkali and filter off the crystals on a Witt filter. On recrystallizing from alcohol large prismatic transparent crystals of terpin hydrate are obtained. M. Pt. 117° C. Now mix 25 grams of terpin hydrate with 50 grams of phosphoric acid ($D = 1.12$) and heat one hour under a reflux. The resulting terpineol is steam distilled and fractionated. It is largely used in perfumery and soap making as it is an agreeable and very cheap perfume.

Reaction:

$$\underset{\text{Terpin hydrate}}{C_{10}H_{18}(OH)_2 \cdot H_2O} + H_3PO_4 = \underset{\text{Terpineol}}{C_{10}H_{17}OH} + 2H_2O$$

Identification Derivative: Terpineol phenyl-urethane, $C_{17}H_{23}O_2N$. At ordinary temperatures molecular proportions of terpineol and phenyl iso-cyanite[1] react to form the phenyl-urethane. M.Pt. 85° C.

Reaction: $C_{10}H_{17}OH + C_6H_5N : CO = C_6H_5NH.COOC_{10}H_{17}$
Terpineol Terpineol phenyl-urethane

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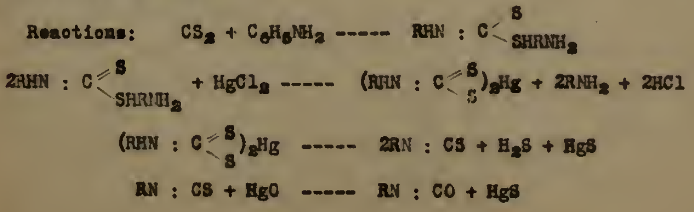
1. Phenyl iso-cyanate may be prepared as follows, by Noyes method: Mix a solution of 20 parts of carbon disulphide in twice its volume of alcohol with 25 parts of aniline. Evaporate off part of the alcohol, and then treat with 39 parts of powdered mercuric chlorid, running it in slowly while stirring. Now add slowly with constant stirring, 30 parts of mercuire oxide. Filter on a Witt filter using double filter papers. Wash the percipitate while filtering with alcohol until a clear solution is obtained. Evaporate to small volume and allow to crystallize.



Reactions: $CS_2 + C_6H_5NH_2 \text{ ----- } RHN : C\genfrac{}{}{0pt}{}{S}{SHRNH_2}$

$2RHN : C\genfrac{}{}{0pt}{}{S}{SHRNH_2} + HgCl_2 \text{ ----- } (RHN : C\genfrac{}{}{0pt}{}{S}{S})_2Hg + 2RNH_2 + 2HCl$

$(RHN : C\genfrac{}{}{0pt}{}{S}{S})_2Hg \text{ ----- } 2RN : CS + H_2S + HgS$

$RN : CS + HgO \text{ ----- } RN : CO + HgS$

SASSAFRAS OIL (Oleum Sassafrassae)

1. Botanical Derivation: Sasafras officinale.

   a. Habitat: North America (Trees 100 feet high in Virginia)

   b. Extraction: Distillation of roots, bark and wood.

   c. Per cent yield: 6 to 9 per cent. (One ton of roots gives one gallon of oil in two days)

2. Physical Properties:

   D_{25} = 1.065 - 1.095 Color: Light-reddish-yellow.

   $n_{d_{20}}$ = 1.5275

   a_d = 0 to +4°

3. Constituents:

Safrol,	80 per cent
Pinene) Phellandrene)	10 " "
D. Camphor,	6.8 " "
Cadinene,	3.0 " "
Eugenol,	0.5 " "

4. Adulterants:

   a. Frequently camphor oil (D = .970)

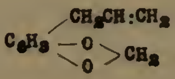
   b. "Artificial Sassafras Oil" which is fractionated camphor oil of 50 per cent safrol content and D = 1.070.

5. Chemical Analysis: Follow the general outline omitting B3b and 4, and including special directions given below, verifying results.

(A) Safrol, $C_{10}H_{10}O_2$.

Definition: It is the methylene ether of allyl dioxybenzene.

Formula:



$$C_6H_3\begin{cases}-CH_2CH{:}CH_2\\ -O\\ -O\end{cases}>CH_2$$

Chief Occurrence: Sassafras, camphor oil, anise.

Detection: Chapman's test (Q.V.)

Physical Properties:

D = 1.100 Color: Light yellow.

$n_{d_{17}}$ = 1.5384 M.Pt. +8° C.

a_d = Inactive. B,Pt. 232° C.

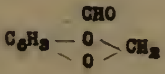
Isolation and Approximate Estimation: Weigh out 100 grams of well dried sassafras oil into a tared beaker, place in a freezing mixture of ice and salt, and stir with a glass rod. After solidification quickly pour off the supernatant liquid, saving it for further analysis. Place the beaker containing the crystals back in the ice, and stir and pat the crystals to a solid cake with a spatula. Pour off the little liquid that has separated, allow the cake to liquefy, and weigh at room temperature, which weight is the approximate amount of safrol present with camphor as an impurity. Now transfer the crude safrol to a distilling flask and catch the fraction 225° to 235° in a tared receiver. This weight represents the approximate percentage of safrol, and subtracted from the previous one, the approximate percentage of camphor is obtained.

Transformation: Safrol to heliotropin; helitropin, $C_8H_6O_3$.

Synonyms: Piperonal, "Artificial Heliotrope."

Definition: It is the methylene ether of protocatechuic aldehyde.

Formula:



$$C_6H_3 \begin{array}{l} CHO \\ -O \\ \diagdown O \end{array} > CH_2$$

Detection: Aldehyde test, (Q.V.)

Physical Properties:

M.Pt. 37°	Colorless crystals whose odor is injured above the melting point, and which must be kept in the dark.
B.Pt. 263°	

Formation: The best yield is obtained, as always in such cases, by converting the allyl or "normal" group into the propenyl or "isomeric" group, which is more readily and completely oxidized.

$$\underset{\text{Allyl}}{CH_2 - CH:CH_2} \xrightarrow{KOH} \underset{\text{Propenyl}}{CH:CH.CH_3} \xrightarrow{O} \underset{\text{Aldehyde}}{CHO} + CH_3COOH$$

Isomerize 65 grams of safrol with a molecular amount of alcoholic potash by boiling under a reflux for a half hour. Having recovered the iso-safrol by steam distillation it is separated, and 50 grams of it are added slowly to a mixutre of 380 grams of sulphuric acid plus 250 grams of potassium dichromate in 800 cc. of water. Heat gently on a water bath to not over 35° C. for four hours. The product is steam distilled and the distillate extracted with ether.

The heliotropin in ethereal solution is then extracted with a concentrated solution of sodium acid sulphite by violent shaking. The crystalline magma is washed with alcohol, pressed with blotting paper, and dissolved in warm water. Excess of dry sodium carbonate is added when the aldehyde is liberated, and floats to the surface. Separate, wash with cold water, and dry. A 10 per cent solution of heliotropin furnishes a strong stock solution for blending.

6. A Brief Detailed Study of the Other Constituents.[1]-- From the super natant liquid remaining after the isolation of the safrol and camphor, shake out the eugenol as benzoyl eugenol. M.Pt. 69°. Dry and fractionate the remainder. Pinene distils over at 155° to 160° and is identified as the nitroso-chloride. M.Pt. 103°. Phellandrene is caught at 160° to 175°, and is identified as the nitrite, (See Parry, p. 22). Cadinene distils over at 260° to 270° to which apply the sesquiterpene test. Note the color, odor and refractive index of all fractions.

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[1] See Gildemeister and Hoffmann's "The Volatile Oils."

BERGAMOT OIL (Oleum Bergamottae)

1. Botanical Derivation: Citrus bergamia.

   a. Habitat: Southern Europe, especially Calabria, Italy.

   b. Extraction: By expression of the fresh peel of the ripe fruit.

   c. Per cent yield: Variable.

2. Physical Properties:

   D_{15} = .882 - 886

   $^{n}d_{20}$ = 1.465 - 1.466

   a_d = +8° to +22°

   Color: Green, due to chlorophyl.

   Sol: 1 to 3 of 80 per cent alcohol.
   If so, it is free from olive,
   orange or turpentine oils.

3. Constituents:

D. Limonene,	45 - 50 per cent
L. Linalyl acetate,	30 - 40 " "
L. Linalol,	6 - 14 " "
Bergaptene,	4 - 6 " "
Octylene	Traces.
Pinene	
Camphene	
Acetic acid	

4. Adulterants:

Turpentine	Decrease the solubility.
Lemon oil	
Orange oil	
Olive oil	
Distilled bergamot	

5. Chemical Analysis: Follow the general outline, omitting B2a and b and 5b, and including the special directions given below, verifying all results. In taking the optical rotation a 50 mm. tube is necessary.

(A) Linalyl Acetate, $C_{10}H_{17}OCOCH_3$.

Synonyms: "Bergamiol", "Artificial Bergamot."

Definition: It is an ester of a terpene alcohol.

Formula: $CH_3.C.(CH_3):CH.CH_2.CH_2.C(CH_3)(OH)CH:CH_2$

Chief Occurrence: Bergamot, lavender, neroli.

Detection: (See general outline)

Physical Properties:

D_{15} = .912 Color: Water-white

a_d = -6°.25" B.Pt. 220°C. (with decomposition)
102°C. at 15 mm.

Isolation: Fractionally distil 100 cc. of the oil. Catch first under ordinary pressure the fraction 165° to 185° (Limonene) then the fraction 185° to 205° (Linalol), and save both for further examination.

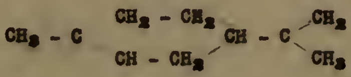
Now continue at reduced pressure catching the fraction 95° to 110° at 15 mm. This is fairly pure linalyl acetate which is sold commercially as "Artificial Bergamot." Much over and under ripe fruit, varying from 6.5 per cent to 45 per cent linalyl acetate is thus utilized in its manufacture, although it is also made by acetylizing linalol and subsequent retification in vacuo.

(B) Limonene, $C_{10}H_{16}$.

Synonyms: "Citrene", "Bergamene", "Carvene", "Hesperidene".

Definition: It is a terpene.

Formula:



Occurrence: Largely in oils from Aurantiaceae and Umbelliferae.

Detection: Burgess' test, (Q.V.). Also as follows: To 5 drops of the original oil add one drop of concentrated hydrochloric acid, plus one drop of concentrated ferric chloride and heat gently.

Color changes: Rose color --- violet red --- blue.

Physical Properties:

D_{20} = .846 B.P. 177°

$n_{d_{20}}$ = 1.4746 a_d = ± 107° [1]

Identification Derivative: Active limonene tetra-bromide, $C_{10}H_{16}Br_4$. Dissolve 10 grams of the limonene isolated in four times its volume of glacial acetic acid, cool in a freezing mixture and gradually add bromine drop by drop until no more is absorbed. Crystals separate rapidly and should be filtered off with the aid of a Witt filter. Press them on a porous plate, and recrystallize from an equal weight of warm acetic ether. M.Pt. 104°.

(C) Linalol, $C_{10}H_{17}OH$.

Synonym: Linalool.

Definition: It is a terpene alcohol isomeric with geraniol.

Formula: $CH_3C(CH_3):CH.CH_2.CH_2.C(CH_3)(OH)CH.CH_2$

Occurrence: Bergamot, lavender, thyme and pititgrain contain L. Linalol. D. Linalol, ("Coriandrol") is found only in coriander.

Detection: Alcohol test, (Q.V.) Also, if boiled with chromic acid, citral is formed which is known by the odor and its b-naptho-cinchonic acid.

Physical Properties:

D_{15} = .870 a_d = -20.7°

$n_{d_{20}}$ = 1.4630 - 1.4690 B.Pt. 197° C.

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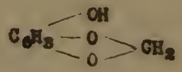
1. Inactive or D-L limonene is called dipentene.

(D) Bergaptene, $C_{12}H_8O_4$.

Definition: It is a "Stearoptene", the monomethyl ether of phloroglucin.

Formula:



$$C_6H_3\begin{matrix} \diagup OH \\ -O \\ \diagdown O \end{matrix}\!\!\!\begin{matrix} \\ > CH_2 \\ \end{matrix}$$

Estimation: Five grams of the oil are weighed into a tared evaporating dish and heated on a water bath at 100° C. until the residue has lost all oder of bergamot. Cool and weigh residue. If more than 6 per cent, some fatty oil, e.g., olive oil, is present. If less than 4 per cent, turpentine, orange or distilled bergamot are present.

Physical Properties:

Soft, white, satiny, odorless crystals. M.P. 188° C.

SPEARMINT OIL (Oleum Mentha Crispae)

1. **Botanical Derivation:** Mentha viridis L., and Mentha Crispa L.

   a. Habitat: North America, Germany, Russia.

   b. Extraction: Steam distillation of the fresh herb.[1]

   c. Per cent yield: 3 per cent

2. **Physical Properties:**

D_{15} = .920 - .940

$n_{d_{20}}$ = 1.4875

a_d = -50° to +48°

Color: Light green.

Sol. 1 to 1 of 90 per cent alcohol.

3. **Constituents:**

Carvone,	35 - 56 per cent.
L. Limonene,	30 - 50 " "
L. Linalol,	5 - 10 " "
L. Pinene,	Traces.

4. **Adulterants:**

Cedarwood oil, revealed by sesquiterpene test.
Gurjun Balsam oil, revealed by sesquiterpene test.

5. **Chemical Analysis:** Follow the general outline, omitting B2a and b, 3b and 4, and including the special directions given below, verifying all results.

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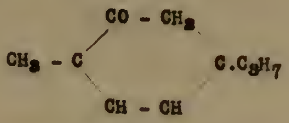
[1] The annual yield from New York and Michigan alone is 12,000 pounds.

(A) Carvone, $C_{10}H_{14}O$.

Synonym: Carvol.

Definition: An aromatic ketone.

Formula:



Occurrence: Spearmint, caraway, dill.

Physical Properties:

D_{15} = .9619 B.Pt. 225°

$n_{d_{20}}$ = 1.5020

a_d = ± 62

Isolation: Through an alcoholic solution of 25 cc. of spearmint oil, which has been saturated with ammonia gas, and which is being cooled by a freezing mixture, pass a stream of hydrogen sulphide gas until crystallization is complete. The resulting crystals of carvone sulph-hydrate (M.Pt. 190°) are purified by recrystallization and decomposed by a slight excess of alcoholic potash when nearly pure carvone is separated, washed, dried and distilled, a very pure product resulting.

Reactions: $C_{10}H_{14}O + H_2S = C_{10}H_{14}(OH)(SH)$

$C_{10}H_{14}(OH)(SH) + C_2H_5OK = C_{10}H_{14}O + KSH + C_2H_5OH$.

Identification Derivatives: Carvoxime, $C_{10}H_{14}NOH$. Ten grams of spearmint oil are dissolved in 25 cc. of 95 per cent alcohol and 5 grams of hydroxylamine hydrochloride, plus 6.5 grams of bicarbonate of soda. The mixture is boiled twenty minutes on a water bath under a reflux. Now add 25 cc. of water and steam distil, continuing until traces of carvoxime crystals appear on the surface of a sample of the distillate which has been collected in a test tube and cooled. The whole is then cooled, and when the oxime has solidified it is collected on a filter, washed, air dried and finally heated for one hour on a water bath, and then the melting point is carefully taken. It should be 72° C.

Carvone tetrabromide, $C_{10}H_{14}OBr_4$. This is obtained by the careful addition of 6.6 cc. of bromine to a cold solution of 10 cc. of D. or L. Carvone dissolved in 10 cc. of glacial acetic acid. Toward the end of the operation the liquid becomes cloudy and very soon solidifies. The crystals are filtered and washed with methyl alcohol, the mother liquor containing an "a" carvone tetrabromide. The crystalline "b" carvone tetrabromide is subsequently dissolved in acetone when upon the addition of a small amount of methyl alcohol it is precipitated in small white orthrhombic crystals (M.Pt. 120° C.). The crystals are optically active and have hemihedral enantimorphous forms which in the case of those obtained from L. carvone have the hemihedral faces in the opposite direction from those derived from D. carvone. (Wallach). This is only one of many instances where the derivative reveals strikingly the exact identity of the original substance.

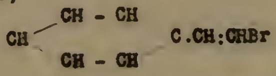
A FEW OF THE MORE COMMON ARTIFICIAL PERFUMES NOT ALREADY DESCRIBED.

I. AUBÉPINE (Hawthorne). Chemically, this is anisic aldehyde, the methyl ether of para-oxybenzaldehyde, $C_6H_4(OCH_3)(CHO)$. It is most easily obtained by warming 25 cc. of aniseed oil with 75 cc. of nitric acid (D. 1.100) for one hour. Separate the heavy oil formed and wash freely with dilute caustic potash. Now agitate the crude oil with a warm concentrated solution of sodium acid sulphite with which the aldehyde combines, and the resulting crystalline magma is washed with alcohol, pressed in heavy German filter paper and dissolved in warm water. Excess of sodium carbonate is added, when the aldehyde is liberated and floats to the surface. Wash, dry and purify further by distillation. Keep it in a dark bottle. Aubépine blends best with orange, neroli and other citrus oils.

$D_{15} = 1.126$ B.Pt. 246°

M.Pt. -4°

II. HYACINTH. The characteristic hyacinth odor is given off by alpha-bromo-styrolene,



$$CH\left\langle\begin{array}{c}CH - CH\\ CH - CH\end{array}\right\rangle C.CH{:}CHBr$$

Styrolene which is phenyl ethylene, $C_6H_5CH = CH_2$, is formed when cinnamic acid is distilled with four times its weight of barium hydrate. Redistil to free from fumes. B.Pt. 144° C.

Reaction: $C_6H_5CH{:}C\,H.COOH \longrightarrow C_6H_5CH{:}CH_2 + CO_2$

Alpha bromo-styrolene is formed by the action of molecular amounts of bromine on styrolene. Use a dropping funnel and condense the hydrobromic acid fumes in water. Purify by distillation. B.Pt. 220°. Fine blends may be obtained with Ylang-Ylang, sandalwood or geranium oils.

III. IMITATION MUSK (Baur). 2-4-6-Tri-nitro 3-Iso-butyltoluene, $C_4H_9.C_6H.(NO_3)_3CH_3$, has a strong odor of musk, especially when mixed with a little ammonium chloride.

Five parts of toluene are mixed with one part of iso-butyl-bromide, and to these are gradually added while boiling, one-fifth part of aluminum chloride. Boil a half hour under a reflux, collecting the hydrobromic acid given off in water. Now reverse the condenser and distil with steam, separate the mixture of iso-butyl-toluene and toluene, dry over anhydrous calcium chloride and fractionate. B.Pt. iso-butyl-toluene, 190° to 195°. B.Pt. iso-butyl toluene, 110°.

Reaction: $C_6H_5CH_3 + C_4H_9Br = C_4H_9.C_6H_4.CH_3 + HBr$

Now mix together three parts of fuming nitric acid, plus six parts of fuming sulphuric acid, and to this mixture carefully add, while cooling, one part of iso-butyl toluene. Each drop causes a violent reaction. As soon as all is added, the mixture is allowed to stand a half hour and then is heated to 100° C. for six hours. After cooling the nitro product is precipitated by pouring into a large amount of cold water, and washed free of acid. It separates first as a heavy oil which, after being distilled with steam to free from uncombined oils, hardens into a firm crystalline body. Purify by recrystallizing from 95 per cent alcohol. M.Pt. 96°

Reaction: $C_4H_9C_6H_4.CH_3 + 3HNO_3 = C_4H_9.C_6H(NO_3)_3.CH_3 + 3H_2O$

"Baur Musk" is soluble to only a limited extent, about 4 per cent dissolving in 90 per sent alcohol.

At the best, imitation musks are poor substitutes for the genuine and proportionately more must be used. A relatively large amount of a delicate and otherwise evanescent perfume is permanently "fixed" by the addition of a few drops of genuine musk, concerning the chemistry of which but little is known.

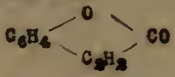
IV. ORANGE-FLOWER (Neroli). The characteristic odor of neroli is due almost wholly to methyl anthranilate, $CH_3COOC_6H_4NH_2$, which is present in very small quantities. It is an "odor bearer."

Ortho-nitro-benzoic acid is formed when one part of benzoic acid is intimately mixed by trituration with one-half part of sand, plus two parts of sodium nitrate, and the mixture is slowly added with stirring to three parts of warm concentrated sulphuric acid. Allow to stand with occasional stirring for a half-hour, and then heat on steam bath until an oil comes to the surface. Pour off the oil into water and distil it with steam. Heat the product to boiling, filter and allow the ortho-nitro-benzoic acid to crystallize. M.Pt., 147°

Anthranilic acid, ortho-amino-benzoic acid, is formed when ortho-nitro-benzoic acid is reduced with calculated quantities of tin and concentrated hydrochloric acid. M. Pt., 144°.

All methyl esters such as methyl anthranilate are formed when a molecular amount of the given aromatic acid is dissolved in an excess of methyl alcohol, and a dry stream of hydrochloric acid gas is passed through. the solution until it is saturated. Then warm to 100° for three hours and precipitate the oil by adding a large quantity of water. Separate, wash, dry and rectify by distillation. Methyl anthranilate has a characteristic blue fluorescence, and an extremely sweet odor. It blends well with Rosemary, lemon, orange or aubépine. M.Pt. 25°; B.Pt. 132° at 14 mm.

V. NEW MOWN HAY (Coumarin). The delightful odor of new mown hay owes its fragrance largely to a chemical body known as coumarin which is the delta lactone of coumarinic acid



Salicylic aldehyde, the mother substance, is easily prepared from phenol. B.Pt. 196°. Coumarin is formed by heating molecular amounts of salicylic aldehyde, acetic anhydride and a little sodium acetate for one hour under a reflux. The whole solidifies to a crystalline mass from which, on treatment with steam acetic acid separates from previously formed aceto-coumarinic acid, leaving coumarin as a product. Coumarin occurs naturally in a large number of wild flowers and plants. It is used largely to impart a lasting sweetness of odor, but there are some oils where the use of vanillin is much to be preferred.

M.Pt. 67° . Sol. 14 to 100 of 90 per cent alcohol.

B.Pt. 290°

VI. NIOBE. The perfume sold under this name is the methyl ether of benzoic acid, $C_6H_5COOCH_3$. Methyl benzoate is prepared by the general method given under methyl salicylate. Dissolve benzoic acid in excess of methyl alcohol, and saturate the solution with dry hydrochloric acid gas. The whole is warmed to 100° for three hours and then considerable cold water added. Separate, wash, dry and rectify the product by distillation. B.Pt. 195° It is a poor blender, and so characteristic that but little can be added without detection. It is used where strong, cheap odors are required, e.g., cheap soaps, and blends best with strong odors such as bitter almond, patchouli or clove.

VII. WINTERGREEN AND SWEET BIRCH. Wintergreen and sweet birch are, chemically, the methyl ether of ortho hydroxy-benzoic acid, $C_6H_4(OH)COOCH_3$.

Methyl-salicylate is prepared in exactly the same manner as niobe, substituting salicylic acid for benzoic acid. If well rectified it may be put to all the uses of the genuine, the difference being that the latter is more delicate of odor. Methyl salicylate is very largely used as it costs about one-tenth of the genuine.

Wintergreen blends well with eucalyptol, (cineol) and such blends are used in certain pharmaceutical preparations.

True oil of wintergreen contains 99 per cent and oil of sweet birch 99.8 per cent of methyl salicylate. All three oils have practically the same characteristics, making it almost impossible to tell them apart.

Phys. Props.	Wintergreen Oil	Birch Oil	Synthetic Methyl Salicylate
D_{15}	1.180 to 1.187	(Same)	(Same)
a_d	$-0^\circ.25''$	0°	0°
Sol.	1 to 5 of 70 per cent alcohol	(Same)	(Same)

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